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Mayanovic, Robert A., R. J. Sladek, and U. Debska. "Ultrasonic propagation-time measurements in Zn 1− x Mn x Se down to low temperatures: Shear-wave anomalies and the spin-glass transition." Physical Review B 38, no. 8 (1988): 5530.

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PHYSICAL REVIEW B VOLUME 38, NUMBER 8 15 SEPTEMBER 1988-I

Ultrasonic propagation-time measurements in $Zn_{1-x}Mn_xSe$ down to low temperatures: Shear-wave anomalies and the spin-glass transition

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(Received 17 February 1988)

Ultrasonic transit-time measurements have been made down to 1.5 K on hexagonal, wurtzite-structured $Zn_{1-x}Mn_xSe$, with $x=0.37$ and 0.53. The velocities of longitudinal waves increased monotonically with decreasing temperature, as expected from the anharmonicity of crystal bonding forces. However, the shear-wave velocities fell below that expected from ordinary anharmonic effects starting at about 150 K and went through a broad, shallow minimum with its lowest point near the spin-glass transition temperature, T_{sg}. The depression was smaller at $x=0.37$ than at $x=0.53$ and smaller at 145 MHz than at 30 MHz. We attribute it to ultrasonic strain-induced modulation of the Mn-Mn superexchange interaction and the concomitant changes in Mn spin-spin correlations involving some kind of anisotropy. Comparison with results on $Cd_{1-x}Mn_xTe$ indicates anion dependence. An analysis is given of our results which employs an empirical expression involving the magnetic susceptibility. The expression was constructed by combining theoretical relations developed by others for ordinary antiferromagnetic materials and for spin glasses. It is inferred that some type of ordering begins near 160 K (associated with isolated spin clusters) in addition to the ordering which begins at the much lower spin-glass temperature.

I. INTRODUCTION

Diluted magnetic semiconductors (DMS) with chemical formulas $A^{II}_{1-x}Mn_xC^{VI}$ exhibit a spin-glass-like transition at some low temperature, T_{sg}, which is higher the larger the Mn content.[1] Since ultrasonic studies can provide information about "ordinary" magnetic phase transitions,[2] investigations were begun, in this laboratory, of the transit times of ultrasonic waves in DMS down to 1.5 K (Refs. 3–5). It was found that in $Cd_{1-x}Mn_xTe$ with $x \gtrsim 0.2$ the shear-wave velocity was less than that expected from the anharmonicity in crystal binding forces over a wide temperature range which extended from far above T_{sg} down to the lowest temperature used. In fact for $Cd_{1-x}Mn_xTe$ with $x \geq 0.35$ the velocity depression went through a broad, shallow minimum with its lowest point near T_{sg}. This effect was related[5] to the magnetic contribution to the heat capacity[6] via thermodynamic considerations and involved both the first- and second-order strain derivatives of a magnetic energy, E_m, which depends on the Mn-Mn exchange interaction. Although the form of the velocity minimum could be accounted for in a qualitative manner, a quantitative fit of the data was not possible, and it was not clear how the ratio between the second- and first-order strain derivatives of the magnetic energy could have the values that were obtained.

Since in the wide-band-gap DMS $Cd_{1-x}Mn_xTe$ the important interaction between Mn ions is due to superexchange via the nearest anion[7,8] and ultrasonic modulation of this interaction seems to be responsible for ultrasonic "anomalies" at low T, we initiated ultrasonic measurements on a wide-band-gap DMS which contained another type of anion, i.e., Se. $Zn_{1-x}Mn_xSe$ was chosen for study, rather than $Cd_{1-x}Mn_xSe$, for example, because of the availability of suitably large crystals of the former but not of the latter.

A preliminary report on the ultrasonic velocity and attenuation in $Zn_{1-x}Mn_xSe$ has appeared[9] and the room-temperature elastic constants[10] and low-temperature attenuation data[11] have been described and analyzed in detail in separate papers with Ref. 11 containing attenuation results on $Cd_{1-x}Mn_xTe$ as well as on $Zn_{1-x}Mn_xSe$.

Herein, we shall present and discuss in detail the results of our measurements of the transit time of pulses of 30 MHz (and also in one case of 145 MHz) ultrasonic waves in $Zn_{1-x}Mn_xSe$ as a function of temperature. Our discussion will combine concepts and formulas used to describe the ultrasonic velocity depression in solids with a paramagnetic-antiferromagnetic transition with ideas about spin-glass-like ordering and spin clustering in spin glasses.

II. EXPERIMENTAL DETAILS

Our $Zn_{1-x}Mn_xSe$ and $Cd_{1-x}Mn_xTe$ samples were obtained from boules grown by one of us (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. A quartz transducer for converting rf to ultrasound was attached to one face of the sample for each set of measurements.

The transit time of 2 μs duration pulses of ultrasonic waves with frequencies between 30 MHz and 150 MHz were determined by methods employed previously in this

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laboratory[10] using commercial electronic instrumentation. The pulse echo-overlap method[12] was used for the transit-time measurements. Temperature was determined with commercial Ge and Pt resistance thermometers with accuracy of 0.1 K above 20 K and of 0.01 K below 20 K.

Data were usually collected with the sample, suspended in a Dewar flask having both liquid He and liquid nitrogen compartments. Above 4.2 K the sample temperature rose at about $\frac{1}{5}$ to $\frac{1}{3}$ degree Kelvin per minute. However, in order to investigate the frequency dependence of the shear velocity minimum in $Zn_{0.47}Mn_{0.53}Se$, both 30 MHz and 145 MHz pulses were used at a series of steady temperatures.

For measurements made above 300 K we used a sample holder encased in a quartz glass tube located in a furnace and determined the temperature with a Chromel-Alumel thermocouple.

III. RESULTS AND DISCUSSION

Determination of the temperature dependence of ultrasonic velocities and elastic constants requires a knowledge of the change of sample dimensions with temperature since $v=2Lf=\sqrt{C/\rho}$ where L and ρ are sample length and density, and C is an elastic constant or combination of elastic constants,[13] and f, the pulse echo-overlap frequency, is the inverse of the transit time. Since thermal expansivity versus temperature data were not available for our samples, we show echo-overlap frequency data in Figs. 1–4. Because of the very small thermal expansivity of cubic ZnSe and of hexagonal ZnS the temperature dependence of the velocity is essentially that of the overlap frequency and the T dependence of the elastic constant (combination) that of overlap frequency squared.

From Fig. 1 we see that the overlap frequency for longitudinal waves propagating along the a axis, f_{11}, and along the c axis, f_{33}, increases monotonically with decreasing temperature as would be expected from lattice anharmonicity.[14] For comparison we note that the longitudinal and the shear elastic constants of cubic ZnSe increase monotonically with decreasing temperature in the range where they have been measured (300 K down to 77 K).

For shear waves also we found an anharmonic type of monotonic increase of overlap frequency with decreasing temperature down to about 160 K. However, from Figs. 2 and 3 it can be seen that at lower temperatures the squared overlap frequency lies below the anharmonic lattice value extrapolated from our higher-temperature data using Lakkad's formula[15] and goes through a broad minimum whose lowest point is near the spin-glass transition temperature [15 K (Ref. 16) for $x=0.37$ and 24 K (Ref. 17) for $x=0.53$]. Furthermore the depression below the anharmonic lattice extrapolation is larger for $x=0.53$ than for $x=0.37$. Careful measurements (see Sec. II) on our $Zn_{0.47}Mn_{0.53}Se$ sample revealed a shear-wave-overlap frequency minimum which was less deep at 145 MHz than at 30 MHz. This is shown in Fig. 4.

In order to interpret the shear-wave velocity or elastic constant minimum implied by the overlap frequency data, we first note that our minimum has some features (such as being less deep at higher frequency) in qualitative accord with formulas developed for spin glasses.[18,19] Unfortunately these formulas predict a velocity depression for longitudinal waves while we observe a depression with shear waves but not with longitudinal waves. Furthermore, the random bond assumption made to represent Heisenberg spins[18] or Ising spins[19] is probably not appropriate for our samples because the interaction between Mn ions is due to superexchange in wide-band-gap DMS,[5,6] whereas real or virtually excited carriers are involved in canonical spin glasses [Ruderman-Kittel-Kasuya-Yosida (RKKY) interaction] and narrow-band-gap DMS (Bloembergen-Rowland mechanism).[20] Another problem for us is that theories[18,19] for ultrasonic velocity

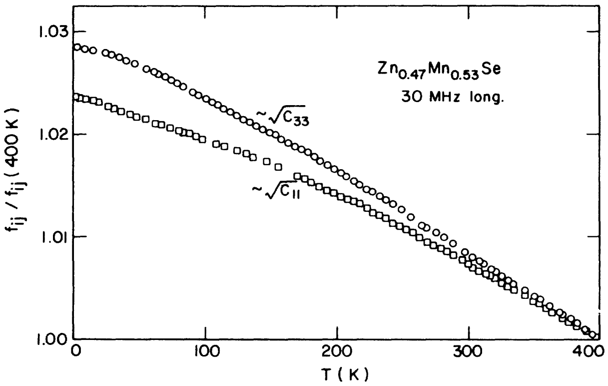

FIG. 1. Echo overlap frequency relative to that at 400 K vs temperature for 30 MHz longitudinal ultrasonic waves propagating along the c axis $(\sim\sqrt{C_{33}})$ and along the a axis $(\sim\sqrt{C_{11}})$ in $Zn_{0.47}Mn_{0.53}Se$.

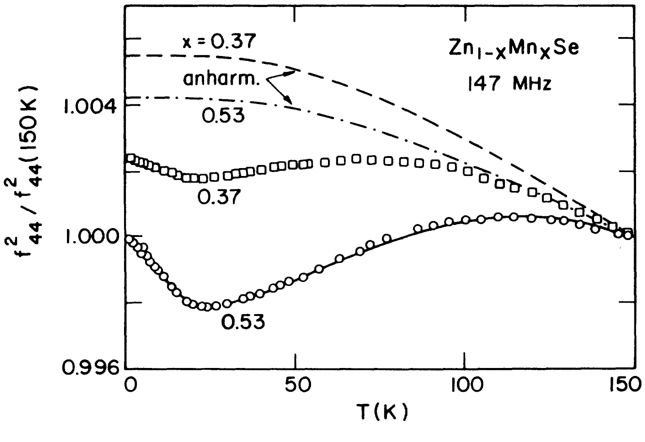

FIG. 2. Echo overlap frequency squared relative to that at 150 K vs temperature for 147 MHz shear ultrasonic waves propagating along the c axis in $Zn_{1-x}Mn_xSe$ with $x=0.37$ and 0.53. The dashed curves show the behavior expected by extrapolating data from 150 K using an anharmonic oscillator model. The full curve is drawn through the $x=0.53$ data points to aid the eye.

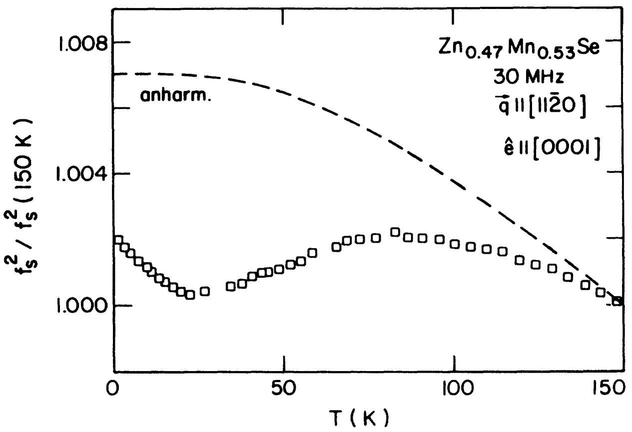

FIG. 3. Echo overlap frequency squared relative to that at 150 K vs temperature for 30 MHz shear ultrasonic waves involving C_{66} in $Zn_{0.47}Mn_{0.53}Se$; **q** and **ê** give the wave propagation and polarization directions, respectively.

in spin glasses predict an attenuation maximum or divergence at T_{sg} which we did not find. Instead we found an attenuation peak[9,21] located almost entirely below T_{sg} with its highest point about 10 K below T_{sg}.

We have been able to construct an empirical formula which can represent qualitatively much of the velocity depression in our samples. Our formula was developed by modifying a formula for the velocity change due to magnetic ions in antiferromagnets.[22,23] The latter formula contains terms depending on the second as well as the first distance derivative of the exchange integral (only terms of the latter type appear in the formula of Ref. 18 because of the random bond assumption employed, therein). Our modification is based on reinterpreting the spin polarization terms due to a magnetic field in Refs. 22 and 23 to make them represent the spin-squared "polarization" in the spin-glass state. To do this we employ an order parameter,[24] $q(T/T_{sg})$, which is zero above T_{sg} but which rises at an ever decreasing rate as temperature decreases below T_{sg} until leveling off and reaching unity at $T=0$. Such an order parameter appears explicitly in one set of terms of the formula for velocity of spin-glasses in Ref. 18.

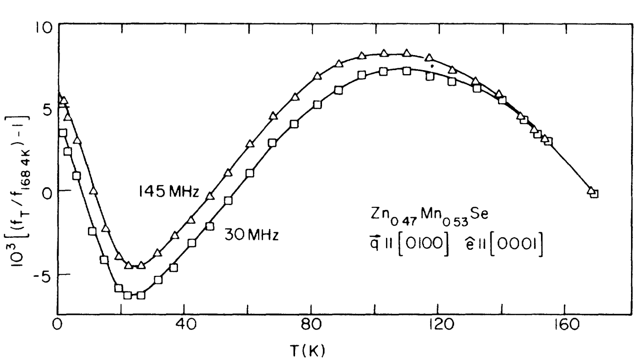

FIG. 4. Fractional change in echo-overlap frequency vs temperature for 30 MHz and 145 MHz shear ultrasonic waves involving C_{44} in $Zn_{0.47}Mn_{0.53}Se$; **q** and **ê** give the wave propagation and polarization directions, respectively. Curves have been drawn through the data points to aid the eye.

The form of our empirical expression is

$$\Delta v = -\frac{1}{\rho V v k^2} \times \left[\left[2g_{\mathbf{k}}^2 \frac{\chi}{(g\mu_B)^2} + \tfrac{1}{2} h_{\mathbf{k}} \right] S(S+1) q(T/T_{sg}) + k_B T \left[g_{\mathbf{k}}^2 \frac{\chi^2}{(g\mu_B)^4} + \frac{h_{\mathbf{k}} \chi}{(g\mu_B)^2} \right] \right] \qquad (1)$$

where ρ and V are crystal density and volume; v and $\mathbf{k}$ are ultrasonic velocity and wave vector;

$$g_{\mathbf{k}}^2 \sim \left[\sum_j n(\mathbf{k}\cdot\mathbf{R}_{ij}) \left[\hat{\mathbf{e}}_{\mathbf{k}} \cdot \frac{\partial J}{\partial \mathbf{R}_i} \right] \right]^2 ,$$

$$h_{\mathbf{k}} \sim \sum_j (\mathbf{k}\cdot\mathbf{R}_{ij})^2 \left[\hat{\mathbf{e}}_{\mathbf{k}} \hat{\mathbf{e}}_{-\mathbf{k}} \frac{\partial^2 J}{\partial \mathbf{R}_i \partial \mathbf{R}_j} \right] , \qquad (2)$$

where $\mathbf{R}_i$ and $\mathbf{R}_j$ are position vectors of neighbor Mn ions, J is the exchange integral, and $\hat{\mathbf{e}}_{\mathbf{k}}$ is the polarization of the ultrasound; $g\mu_B$ is the Landé g-factor Bohr magneton product, S is the $\frac{5}{2}$ spin of the Mn^{2+} ion, $k_B T$ is the Boltzmann constant times absolute temperature, $q(T/T_{sg})$ is the spin-glass order parameter mentioned above, and χ is the magnetic susceptibility which is frequency dependent as inferred from there being less of a velocity depression at 145 MHz than at 30 MHz and from the attenuation maximum which we have observed below T_{sg}.[9,11,21]

Reference 23 and references cited therein should be consulted for the formula for antiferromagnets and to acquire an appreciation for how it was obtained by treating the correlation between spins which is affected by ultrasonic modulation of the exchange interaction. In spin-glasses such correlations have to be treated differently[24] than in antiferromagnets.

We now indicate how Eq. (1) can account quantitatively for various features of our shear-wave-velocity depression and we shall then suggest an additional modification needed to "cut off" the depression at high T (near 160 K).

At lowest T, we expect χ to be negligible because from our attenuation results[11,12] we expect it to be proportional to $\{T[(\omega\tau)^{-m}+(\omega\tau)^{1-n}]\}^{-1}$ where m and $1-n$ are less than one and $\tau=\tau_0\exp(E/k_B T)$. Thus $\omega\tau$ becomes very large at lowest T and all χ-containing terms become negligible. However, Eq. (1) predicts that some velocity depression remains at low T because of the term not containing χ. This accords with our observation that the shear-wave echo-overlap frequency (see Figs. 2–4) and hence velocity is still below the anharmonically expected value at 1.5 K. With increasing T, χ increases at first more than $q(T/T_{sg})$ decreases. The decrease in χ is due to the decrease in $\omega\tau$. In this range both the $q(T/T_{sg})$-containing terms and the $k_B T$-containing terms contribute to the depression. However, as T increases further, $q(T/T_{sg})$ decreases more than χ can rise so that the depression due to $q(T/T_{sg})$-containing terms decreases rapidly and then disappears near T_{sg}. However, the $k_B T$-containing terms still cause depression. Above T_{sg}, χ decreases with increasing T and the depression is controlled by the competition between the increase in $k_B T$ and the decrease in the dc susceptibility. As a consequence Eq. (1) predicts that some depression should persist to far above T_{sg} as indeed does occur in our samples. However, since the $\chi_{dc} \sim 1/[T+\theta(T)]$ and $\theta(T)$ is always greater than T and increases to ~ 955 K (Ref. 25) somewhere above 200 K, Eq. (1) predicts that a velocity depression would persist to even higher temperatures than where the measured depression disappears at about 150 or 160 K. We suggest that the $k_B T$-containing terms should have included another order parameter factor which goes to zero near ~ 160 K. We have been able to fit data for our $x=0.53$ sample with an *ad hoc* expression[11,21] which has terms containing such an order parameter as well as terms containing the spin-glass order parameter which is zero above about T_{sg}.

The high-T order parameter might indicate that spins begin to freeze into isolated clusters or domains as the temperature drops below ~ 160 K. The freezing becomes more extensive as T decreases further until the spin-glass transition occurs. Although definitive evidence for clusters or domains in our samples is not available, as far as we know, neutron diffraction studies[26] on $Zn_{1-x}Mn_xTe$ and $Zn_{0.45}Mn_{0.55}Se$ reveal a tendency toward antiferromagnetic ordering of type III. This was attributed to magnetic scattering by Mn spins surrounded by near-neighbor shells of correlated spins. Additional indications that clusters or domains may be present in DMS could be the departure of the magnetic susceptibility from a Curie-Weiss behavior at temperatures 15 to 20 times T_{sg} in various DMS (Ref. 27) and a broad heat capacity maximum[28] with its highest point occurring well above T_{sg} (where T_{sg} is obtained from the cusp in χ). Some χ and heat capacity data on DMS have been interpreted in terms of there being some disorder below T_{sg} due to finite (antiferromagnetic) clusters which are separate from the infinite cluster and some order above T_{sg} due to the persistence of some finite clusters.[29] Different behaviors have been attributed to spins "frozen" within clusters and of "free" spins in regions where internal fields from different neighbors cancel. Perhaps the intracluster and intercluster interaction model for metallic spin-glass alloys[30] (which have long-range interactions between Mn spins due to mobile electrons) could be reinterpreted to describe the "frozen" and "free" spins in wide-band-gap DMS in which the interaction between Mn spins is short range since it arises from superexchange via the anion.

Because of the frequency dependence of χ, the χ-dependent terms in Eq. (1) can account qualitatively for the smaller velocity depression at 145 MHz than at 30 MHz implied by our echo-overlap frequency data in Fig. 4.

The occurrence of a velocity depression for shear waves but not for longitudinal waves in both $Zn_{1-x}Mn_xSe$ and $Cd_{1-x}Mn_xTe$ merits special attention because this behavior is unlike that observed in ordinary antiferromagnets or that predicted by theories for ultrasound in spin-glasses.[18,19] The shear wave velocity depression in DMS seems to require the derivatives of the Mn-Mn exchange interaction have some kind of anisotropy. This might be associated with spin-orbit coupling on the anion,[31] distortion of the Mn—C^{VI}—Mn bond angle, or with nonisotropy in the distribution of nearest or next-nearest-neighbor (NNN) Mn ions or in the orientations of the NNN spins. The latter might be a consequence of the clustering mentioned above.

Inclusion of spin-orbit coupling in the superexchange mechanism gives the Dzialoshinski-Moriya (DM) anisotropic superexchange[32] with strength $D \sim \lambda J/U$ where λ is the spin-orbit coupling on the anion, J is the superexchange integral (see Ref. 7), and U is the separation between the filled and empty Mn $3d$ energy levels. Evidence for anisotropic superexchange has been deduced from EPR experiments[31] on Cd-based DMS and attributed to the DM interaction. This implies that D should replace J in Eqs. (2) and (3). However, since λ and U are relatively insensitive to strain, ϵ, the net result would be for each J derivative to be multiplied by λ/U. Since $\lambda_{Se}/\lambda_{Te} \approx 0.46$,[33] a smaller shear wave velocity minimum would be expected in $Zn_{1-x}Mn_xSe$ than in $Cd_{1-x}Mn_xTe$, provided that $\partial^2 J/\partial \mathbf{R}_i \partial \mathbf{R}_j$ has the appropriate sign. We do observe a smaller minimum in $Zn_{1-x}Mn_xSe$ than in $Cd_{1-x}Mn_xTe$.

Ultrasonic distortion of the Mn—C^{VI}—Mn bond angle would most likely exert its influence because of strain dependence of the anion npMn $3d$ hybridization energy, V_{pd}, since $J \sim V_{pd}^4$ (Ref. 25).

In summary, we have found that below ~ 160 K the velocities of shear, but not of longitudinal, ultrasonic waves in $Zn_{1-x}Mn_xSe$ are less than those expected from an anharmonic extrapolation of higher- temperature data and go through a minimum whose lowest point is near the spin-glass transition temperature. The effects are interpreted in terms of ultrasonic modulation of the anion-mediated superexchange interaction between Mn ions and the accompanying change in correlations between Mn spins. Some ordering process seems to begin at temperatures far above where the spin-glass transition occurs.

ACKNOWLEDGMENTS

This work was supported in part by the National Science Foundation via Purdue University Materials Research Laboratory Grants No. DMR-83-16988 and No. DMR-84-18453. Thanks are due to Professor J. K. Furdyna for making samples available to us and to him and Professor J. Spałek for stimulating discussions.

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