to Eq. (1) given some inherent $\Delta k_{\parallel}$. A rough estimate which accounts for most of the observed width at $E_B = 0$ is $\Delta k_{\parallel} = 0.03-0.04$ Å^{-1}, implying a real-space scattering length of 20–30 Å. This length is not consistent with that derived from LEED results which require coherent scattering from much larger domains. Defect or phonon scattering could destroy the coherence of the photoemission initial or final state without affecting the long-range order required to produce sharp LEED beams. 20–30 Å is a reasonable estimate of the average separation of defects and impurities. The surface is then viewed as a dilute alloy of defects and impurities in copper, for which the momentum would be ill defined. The sputtered surface results are nicely explained in these terms.[9] The effect of phonons is less straightforward. A simple Debye-Waller effect[15-17] does not explain the results completely. While it might account for the observed temperature dependence of the intensity and width, that of the peak energy is not easily included. More significantly, an extrapolation to zero temperature yields a result very close to the room-temperature curve, implying that Debye-Waller broadening provides only a small contribution. A rough estimate of the Debye-Waller factor at these energies and temperatures[15] confirms this result.[9] However, evidence for the importance of phonons at higher temperature is provided by these and other[5,7,16,17] results. Several mechanisms—Debye-Waller broadening, lattice expansion, wavefunction renormalization—might be operative.

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[1]J. B. Pendry, in *Photoemission and the Electronic Properties of Surfaces* (Wiley, New York, 1978).
[2]D. E. Eastman, J. A. Knapp, and F. J. Himpsel, Phys. Rev. Lett. 41, 825 (1978).
[3]J. A. Knapp, F. J. Himpsel, and D. E. Eastman, Phys. Rev. B 19, 4952 (1979).
[4]P. Thiry, D. Chandesris, J. Lecante, C. Guillot, R. Pinchaux, and Y. Petroff, Phys. Rev. Lett. 43, 82 (1979).
[5]S. D. Kevan and D. A. Shirley, Phys. Rev. B 22, 542 (1980).
[6]P. O. Gartland and B. J. Slagsvold, Phys. Rev. B 12, 4047 (1975).
[7]J. A. Knapp, F. J. Himpsel, A. R. Williams, and D. E. Eastman, Phys. Rev. B 19, 2844 (1979).
[8]P. Heimann, J. Hermanson, H. Miosga, and H. Neddermeyer, Surf. Sci. 85, 263 (1979).
[9]J. D. Tersoff, S. D. Kevan, and D. R. Hamann, to be published.
[10]N. V. Smith and S. D. Kevan, Nucl. Instrum. Methods 195, 309 (1982).
[11]S. G. Louie, P. Thiry, R. Pinchaux, Y. Petroff, D. Chandesris, and J. Lecante, Phys. Rev. Lett. 44, 549 (1980).
[12]M. R. Halse, Philos. Trans. Roy. Soc. London, Ser. A 265, 507 (1969).
[13]J. J. Quinn, Phys. Rev. 126, 1453 (1962).
[14]P. Nozieres, *The Theory of Interacting Fermi Systems* (Benjamin, New York, 1967).
[15]N. J. Shevchik, Phys. Rev. B 16, 3428 (1977).
[16]R. S. Williams, P. S. Wehner, J. Stöhr, and D. A. Shirley, Phys. Rev. Lett. 39, 302 (1977).
[17]P. Heimann and H. Neddermeyer, Solid State Commun. 26, 279 (1978).

Evidence for the Existence of Magnetic Two-Level Systems in Amorphous Spin-Glasses

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Susceptibility and remanence as well as the phonon thermal conductivity κ^{ph} are studied as a function of temperature and magnetic field on amorphous spin-glasses $(PdCuSi)_{90}TM_{10}$, TM = Mn, Fe, Co. For the Fe and Co alloys $\kappa^{ph}(T)$ is enhanced in a field of 5 T below T_g. The results give evidence for thermal activation of cluster moments (magnetic two-level systems) by inelastic scattering of phonons, coupled via spin-orbit interaction to the magnetic two-level systems. Contributions of spin-wave-like excitations to $\kappa^{ph}(T,H)$ cannot be detected.

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It is well known that magnetic, crystalline spin-glasses reveal some physical properties at low temperatures which are analogous to properties of amorphous materials. Spin-glasses show, e.g., a linear temperature dependence of the magnetic specific heat and characteristic time

dependences in their remanent behavior. It was therefore proposed[1] to describe the low-temperature behavior of spin-glasses in terms of magnetic two-level systems (MTLS), analogous to the structural two-level systems (TLS) introduced for the understanding of the properties of amorphous, nonmagnetic materials.[1,2]

The question of the origin and nature of MTLS in spin-glasses is presently investigated especially from the theoretical side.[3,4] It is assumed that MTLS are associated with regions of complex spin arrangements—magnetic clusters —whose free rotations are blocked by anisotropy energy barriers. Thus, one expects the dynamics of a spin-glass (or cluster glass) to be dominated by thermal activation processes. Experimentally, the presence of MTLS has been mostly shown indirectly, e.g., by relaxation measurements of the remanence.[5,6]

In the present paper we will demonstrate directly the presence of MTLS in amorphous *metallic* spin-glass systems. In studies of the thermal conductivity of (PdCuSi) with Mn, Fe, and Co impurities in various concentrations we will show that MTLS can be activated over their energy barriers by inelastic scattering of phonons. Our work also gives clear insight into the kind of coupling of the phonons to the MTLS as well as knowlegde about the nature of the MTLS.

The samples $(Pd_{67.5}Cu_6Si_{16.5})TM_{10}$, with transition metals (TM) Mn, Fe, and Co, are prepared by the splat-cooling technique.[7] The amorphous state is confirmed by Mo $K\alpha$ x rays and by measurement of the residual resistivity. The magnetic properties (susceptibility and remanence) are also investigated. The heat conductivity is measured by a stationary method on packets of five strips of amorphous material in a He^3 cryostat, incorporating also a 6-T superconducting magnet. Details have been given earlier.[8] Compared with the former measurements[8] the relative accuracy in the determination of $\kappa(T)$ has been increased to a value better than ±0.3% mainly by increasing the accuracy of the calibration of the carbon thermometers in the magnetic fields. The uncertainty in the geometry limits the absolute accuracy of the measurements to ±3%. The phonon contribution $\kappa^{ph}(T)$ is obtained by application of the Wiedemann-Franz law.

Figure 1 shows the phonon thermal conductivity versus temperature T in double logarithmic scale for (PdCuSi) containing 10 at.% Mn. The filled circles represent the data as taken in zero field; the open squares are the data as taken in a field of 5 T. Note that for this sample there is *no* difference in $\kappa^{ph}(T)$ for zero field and in a field of 5 T. Figure 2 exhibits an equivalent presentation of $\kappa^{ph}(T)$ for a sample containing 10 at.% Fe. One can see that for this alloy the thermal conductivity in a 5 T field is enhanced by a maximum of 5% at temperatures below 4 K. This enhancement lies well above the relative accuracy limit of the measurements. Figure 3 shows $\kappa^{ph}(T)$ for a sample containing 10 at.% Co. This figure clearly reveals that in the temperature range below the freezing temperature T_g the conductivity in a 5-T magnetic field is appreciably enhanced (roughly by 10%) as compared with the zero-field behavior. Further measurements have shown that the magnetic contribution is not saturated in 5 T. This is the first time that field enhancements of $\kappa^{ph}(T)$ have been observed for *metallic* amorphous materials. Recently an enhancement of the phonon thermal conductivity on an *insulating*, single-crystalline EuSrS spin-glass sample has been reported, also giving evidence for scattering of phonons from magnetic excitations.[9]

The increased conductivity in a magnetic field

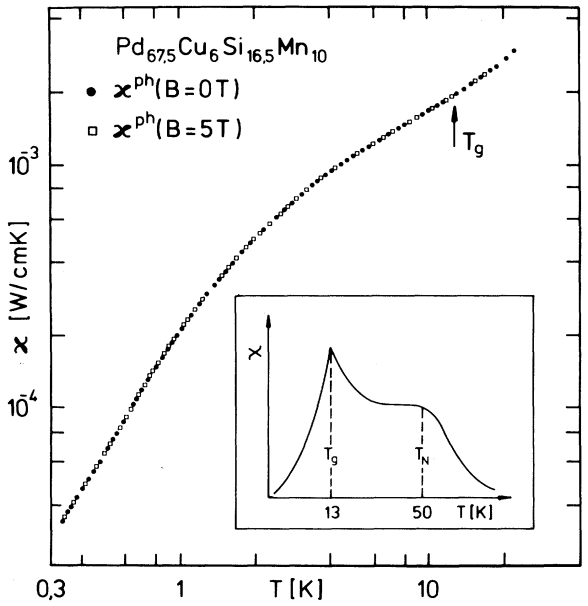

FIG. 1. Phonon thermal conductivity κ^{ph} vs temperature in double logarithmic scale for an amorphous alloy of (PdCuSi) and 10 at.% Mn in zero field (dots) and in a magnetic field of 5 T (open squares). The inset shows the temperature dependence of the susceptibility for the same sample (T_N, transition temperature into an antiferromagnetically ordered state; T_g, spin-glass freezing temperature).

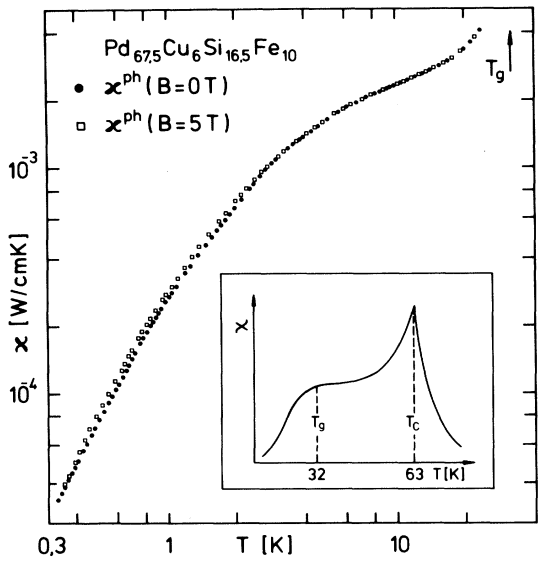

FIG. 2. κ^{ph} vs temperature for an amorphous alloy of (PdCuSi) and 10 at.% Fe in zero field (dots) and a magnetic field of 5 T (open squares). The inset shows the ac susceptibility vs temperature (T_c, transition temperature into a ferromagnetically ordered state; T_g, spin-glass temperature).

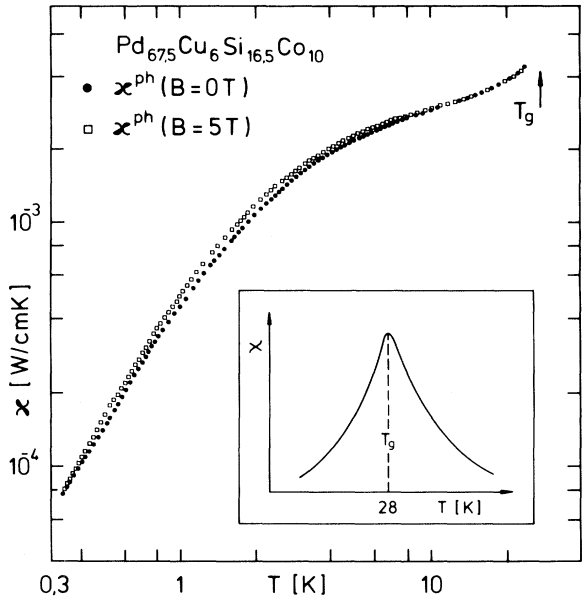

FIG. 3. κ^{ph} vs temperature for an amorphous alloy of (PdCuSi) and 10 at.% Co in zero field (dots) and a magnetic field of 5 T (open squares). The inset shows the temperature dependence of the dc susceptibility (T_g, spin-glass temperature).

cannot originate from a field dependence of the electronic part of $\kappa(T)$. The magnetoresistance for all samples is smaller than 2%, and the electronic contribution to the total thermal conductivity is at maximum of the order of 50%.

The insets in Figs. 1 to 3 show qualitatively the temperature dependence of the zero-field susceptibilities as measured for the respective alloys. The Mn and Fe samples reveal characteristic magnetic double transitions with an antiferromagnetic-like ordering temperature at T_N in Mn, and a transition into a weak ferromagnetically ordered state at T_c for Fe. At lower temperatures for both alloys a second transition into a spin-glass or cluster-glass-like state at T_g follows. For the Mn sample this spin-glass transition is characterized by a sharp cusp at $T_g = 13$ K, whereas for the Fe alloy the spin freezing process is marked by a strong decrease of χ_{ac} below $T_g \approx 30$ K.[10] The 10-at.%-Co sample (Fig. 3) shows only a single-peak spin-glass (or cluster-glass) transition at $T_g = 28$ K. Since we concentrate here more on the thermal transport, the magnetic properties of the samples will be discussed in detail elsewhere.[10] Note, however, that the field enhancements of $\kappa^{ph}(T)$ for Fe and Co occur in temperature regions where the alloys are magnetically in the cluster-glass state, i.e., for $T < T_g$. This point will be important when discussing the physical origin of the enhancement, as shown below.

For the discussion, we first focus on the possible coupling mechanisms between phonons and magnetic excitations in general. This coupling can be achieved either by a modulation of the magnetic exchange interaction between the impurities by the phonons[11] or by an indirect coupling of the moments to the lattice via spin-orbit interaction. We think that our series of results from Mn to Co (Figs. 1–3) clearly demonstrates that the coupling must be of *ls* type. There is no enhancement of $\kappa^{ph}(T)$ in a magnetic field for *S*-state Mn. There is a small enhancement of the thermal conductivity in a field when adding Fe. Fe has a small orbital contribution to the effective moment. There is strong enhancement for Co, which has an orbital component 2 times larger than Fe. This result is supported by electron-spin-resonance measurements on the same samples.[12] The width of the ESR absorption spectra increases when going from Fe to Co reflecting the growing influence of the orbital contribution to the magnetic moments.

Concerning the question of the nature of the magnetic excitations we can get some information from another series of $\kappa^{ph}(T)$ measurements

which we have done on amorphous (PdCuSi) with various concentrations of Fe. The results are given in Fig. 4. The left-hand part of this figure shows the phonon thermal conductivity κ^{ph} versus $\ln T$ for 10 at.% Fe (repeating, for comparison, Fig. 2) and additionally $\kappa^{ph}(T)$ for (PdCuSi) with 15 and 20 at.% Fe. Again, the dots give the thermal transport in zero field, while the open squares exhibit $\kappa^{ph}(T)$ as measured in 5 T. In the right-hand part of Fig. 4 we present the corresponding magnetic measurements, i.e., $\chi(T)$ for 10 and 15 at.% Fe and the spontaneous magnetization M_s versus $T^{3/2}$ for the ferromagnetic sample with 20 at.% Fe. Concerning the thermal conductivity the results in Fig. 4 reveal that the field effect roughly doubles from 10 to 15 at.% Fe, i.e., when for both alloys we remain in the cluster-glass region as the left-hand part of Fig. 4 shows. Surprisingly, for 20 at.% Fe, we do not observe any influence of a magnetic field on $\kappa^{ph}(T)$. This result clearly demonstrates that

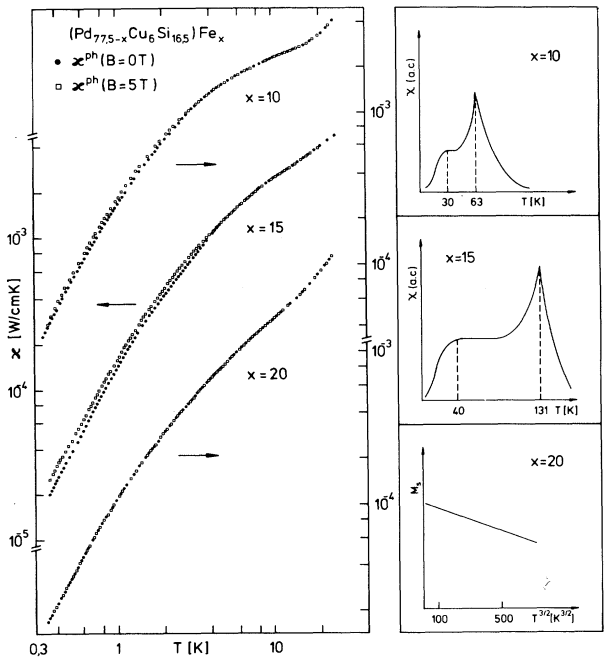

FIG. 4. Left-hand part: Phonon thermal conductivity κ^{ph} vs temperature for a series of $(Pd_{77.5-x}Cu_6Si_{16.5})$ Fe_x alloys with $x = 10, 15, 20$, in zero field (dots) and a magnetic field of 5 T (open squares). Right-hand part: Temperature dependence of the ac susceptibility for the respective alloys with $x = 10$ and 15. Note the magnetic double transitions with the corresponding high-temperature values (T_c) and the lower freezing temperatures T_g. For the ferromagnetic $x = 20$ sample the spontaneous magnetization M_s vs $T^{3/2}$ is given.

scattering of phonons from spin-wave-like excitations *cannot* be the origin of the conductivity enhancement, since this sample is definitely ferromagnetic and there is evidence for the existence of spin-wave-like excitations, as the behavior $M_s \propto T^{3/2}$ shows (see right-hand part of Fig. 4).

Blocking of single spins (with moment μ_s) also does not explain the observed enhancement, because at temperatures of typically 10 K and fields of 5 T the thermal energy $k_B T$ is high as compared with the magnetic energy $\mu_s H$. Further support comes from findings on a 15% Co cluster-glass sample ($T_g \approx 40$ K)—not shown here—where a field enhancement of $\kappa^{ph}(T)$ of more than 7% is still observed at temperatures above 25 K.

Instead, we think that the field enhancement is due to the scattering of phonons from cluster moments. We get evidence for this assumption from the detailed magnetic studies,[10] where the behavior of the thermal remanent magnetization (TRM) as function of temperature and time can only be explained if one assumes the existence of thermal activation of cluster moments over anisotropy barriers. Time effects are only observed in the low-temperature cluster-glass state of the alloys, i.e., below T_g and not in the ferromagnetic range between T_g and the upper critical temperature T_c (see, e.g., Fig. 2).

In the theoretical models[4,5] a simple physical picture for the activation of cluster moments is given. The clusters have two equilibrium positions, with the moments pointing either parallel or antiparallel to the axis of easy magnetization. Both positions are separated by an anisotropy barrier. Such an arrangement is described as a MTLS. The general validity of this MTLS picture is further supported by the successful description of magnetization measurements on a variety of other spin-glass (cluster glass) systems.[5]

Finally, the phonons in our systems have typical relaxation times of $\tau_{ph} \approx 10^{-7}$ sec at 1 K. The closer the relaxation times of the MTLS to τ_{ph} the better the coupling. For single spins one can estimate relaxation times to be of the order of 10^{-11} sec (for 5 T). In contrast to this, measurements of the TRM as a function of temperature and time on crystalline spin-glasses reveal relaxation times of cluster moments of the order of 10^{-6} sec,[6,13] i.e., of the same order of magnitude as τ_{ph}. This argument is a further proof to our assumption that the field enhancement of

$\kappa^{ph}(T)$ is caused by inelastic scattering of phonons from MTLS.

The present findings have some important consequences. From our investigations of the temperature dependence of the magnetic part of $\kappa^{ph}(T)$ it follows that the density of states as a function of energy of the MTLS depends on the kind of magnetic impurity and its concentration. For further analysis measurements of the specific heat in a magnetic field on these materials would be helpful. These measurements would allow a quantitative determination of the coupling constants. Also a detailed investigation of the temperature dependence of the magnetic specific heat is necessary. From these measurements we expect more insight into the problem of whether the sometimes observed linear behavior of $c_m(T)$ at low temperatures originates from spin-wave-like excitations or from excitation of MTLS as the present work proposes. Finally, it would be interesting to calculate theoretically the spin-orbit coupling between phonons and MTLS, a work which simultaneously would lead to an extension of the present cluster models.

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[1]P. W. Anderson, B. I. Halperin, and C. M. Varma, Philos. Mag. 25, 1 (1972).
[2]W. A. Phillips, J. Low Temp. Phys. 7, 351 (1972).
[3]J. Vallain, J. Phys. C 10, 4793 (1977).
[4]C. Dasgupta, S. K. Ma, and C. K. Hu, Phys. Rev. B 20, 3837 (1979).
[5]J. J. Préjean and J. Souletie, J. Phys. (Paris) 41, 1335 (1980).
[6]F. Holzberg, J. L. Tholence, and R. Tournier, in *Proceedings of the Second International Symposium on Amorphous Magnetism, Troy, New York, 1976,* edited by R. A. Levy and R. Hasegawa (Plenum, New York, 1977), p. 1.
[7]The authors are very much indebted to Professor H. J. Güntherodt for sample preparation.
[8]D. M. Herlach, E. F. Wassermann, and J. Kästner, Phys. Rev. B 24, 3204 (1981).
[9]C. Arzoumanian, P. A. de Goer, B. Salce, and F. Holzberg, to be published.
[10]A. Heller, D. M. Herlach, J. Kästner, and E. F. Wasserman, to be published.
[11]K. H. Fischer, Z. Phys. B 43, 291 (1981).
[12]P. Monod and E. F. Wasserman, unpublished.
[13]H. v. Löhneysen and J. Tholence, Phys. Rev. B 19, 5858 (1979).

Electron-Nuclear Double-Resonance Determination of the ^{13}C and ^{1}H Hyperfine Tensors for Polyacetylene

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Pristine 98% ^{13}C-enriched *cis*-polyacetylene has been investigated by electron-nuclear double-resonance spectroscopy at temperatures between 77 and 300 K. Spectra are characterized by two and only two ^{1}H and ^{13}C hyperfine tensors. The relative magnitudes and symmetry of the tensor elements established that the paramagnetic electron resides in a delocalized π orbital. Experimental results indicate that the delocalized electron is constrained to a potential well of approximately 100 Å width.

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Extensive interest in polyacetylene, $(CH)_x$, has been generated by the proposal[1,2] that domain-wall kinks in the electron charge-density wave, analogous to topological solitons, exist in the *trans* isomer of this material. The domain wall is spread over 15 lattice sites and associated with