phonon wind is entirely responsible for the droplet motion. Finally, we feel that the results reported here, together with those reported in Ref. 10, where we showed that high-frequency phonons do not participate in phonon wind, give convincing evidence for the validity of Keldysh's model.

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Magnetic Properties of Liquid Pd, Si, and Pd-Si Alloys

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The magnetic susceptibility χ of liquid Pd, Si, and Pd-Si alloys was measured. For crystalline semiconducting Si, χ changes at the melting point T_M from diamagnetic to paramagnetic values in good agreement with existing theoretical calculations for the liquid state. For liquid Pd, χ is discussed within the Stoner-Wohlfarth and Edwards models. The data obtained for liquid Pd-Si alloys provide an understanding of the diamagnetism of the metallic glass $Pd_{81}Si_{19}$ and will be discussed in the light of recent density-of-states data obtained by photoemission.

The aim of this Letter is twofold. *Firstly*, we are interested in the magnetic properties of the pure liquid metals, Pd and Si. Up to now no experimental data have been available on χ of liquid Pd. On the other hand Pd, in the solid state, is an example where many attempts have been made to understand the magnetic properties.[1] Therefore, the question arises as to the extent to which these theories can be extended to higher temperatures and eventually into the liquid state. The older χ data of liquid Si[2] seem unreliable. It was found by resistivity measurements that Si shows a change at T_M towards metallic conductivity, but no quantitative information on the number of conduction electrons could be extracted. Moreover, the older diamagnetic χ data disagree strongly with theoretical calculations[3] for the liquid state assuming four conduction electrons and taking into account electron-electron interaction. For most of the simple liquid metals these calculations are in good agreement with experiments. Therefore, we remeasured very carefully the magnetic susceptibility of liquid Si and present the first accurate and reliable data.

Secondly, in order to understand the diamagnetism of metallic Pd-Si glasses[4] it seems appropriate to investigate the Pd-Si alloys over the entire concentration range in the liquid state. It was thought that an extrapolation from the liquid into the glassy state would provide an understanding of the behavior of the metallic glasses. Metallic glasses are the subject of an increasing research effort. The interpretation of the properties of metallic glasses presents a particular challenge since the understanding of solid materials has, in the past, generally been based upon their crystal periodicity. The lack of lattice structure in amorphous and liquid metals opens up a new field for the understanding of electronic structure and magnetic properties. The Pd-Si system, forming metallic glasses around $Pd_{80}Si_{20}$, has become a canonical metallic glass, for which very detailed studies of a variety of properties have been undertaken.

We report the first accurate and reliable measurements of χ of Pd and Si in the high-temperature solid and liquid states up to 1700°C. The measurements were performed with a novel high-temperature, high-vacuum pendulum balance operating in a Faraday configuration of the magnetic field. The main emphasis for designing this apparatus was to achieve temperatures above 2000°C. The force exerted on the sample in the magnetic field is compensated by an electromagnetic force. The position of the pendulum is measured with high accuracy and resolution by using a laser beam and a photopotentiometer. The absolute accuracy is estimated to be 2%, whereas the relative accuracy is 1%. The liquid Pd and Pd-Si samples were contained in alumina (Al_2O_3) while the liquid Si samples were kept in beryllia (BeO) crucibles. Measurements were performed in both increasing and decreasing temperatures. Each datum point at a particular temperature represents the average of up to 30 measurements. The average values were then used in a least-squares fit to determine the curves shown in the following figures. The measurements on several different samples of Pd, Si, and the indicated concentrations of Pd-Si were in good agreement within the experimental error. More experimental details will be reported elsewhere.[5]

Figure 1 shows the temperature dependence of χ for Si in the high-temperature solid and liquid states. For crystalline Si, χ is diamagnetic and only weakly T dependent and changes at the melting point to paramagnetic values in the liquid state. This result demonstrates in a nice way a semiconductor-metal transition upon melting.

Figure 2 shows the inverse of χ for Pd in the high-temperature solid and liquid states. The magnetic susceptibility is strongly temperature dependent, following essentially a Curie-Weiss law. At T_M there is only a very small change of 7%. The magnetic susceptibility and the temperature derivative of its inverse for Pd measured above and below T_M are given by $(\chi_A)_{\text{liq}} = 1.076$, $(\chi_A)_{\text{sol}} = 1.148$ [10^{-4} cm^3/g atom] and $(d\chi_A^{-1}/dT)_{\text{liq}} = 2.87$, $(d\chi_A^{-1}/dT)_{\text{sol}} = 4.95$ [g atom/cm^3·K]. Our

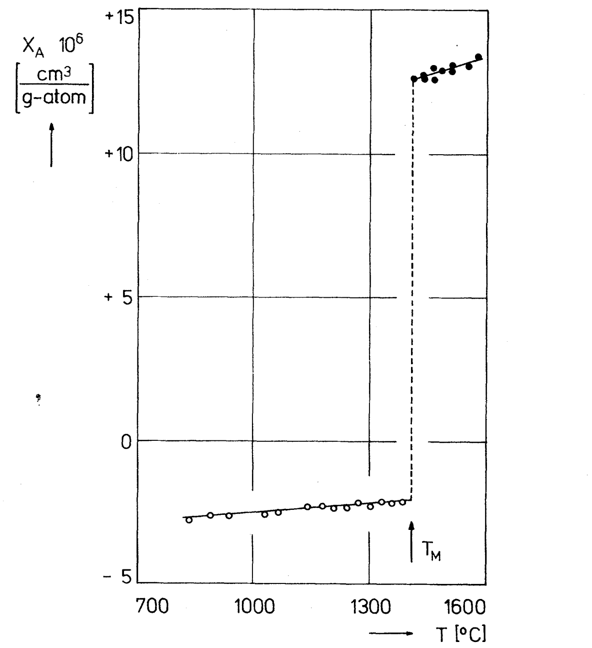

FIG. 1. Magnetic susceptibility of Si at high temperatures.

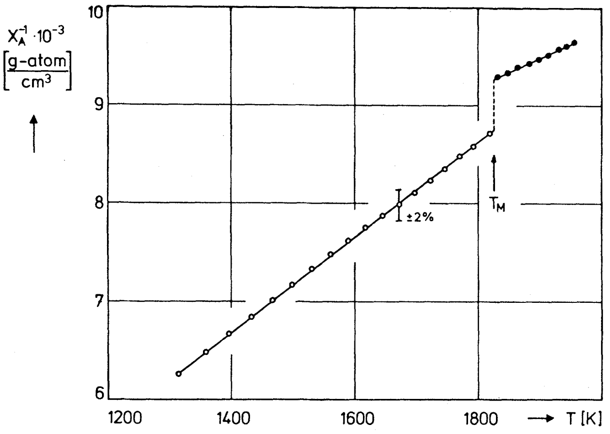

FIG. 2. Inverse magnetic susceptibility of Pd at high temperatures.

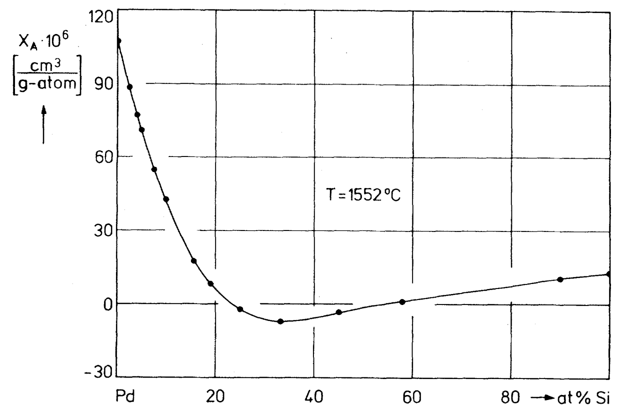

FIG. 3. Magnetic susceptibility of liquid Pd-Si alloys as a function of concentration.

measurements at lower T in the solid state are in reasonable agreement with the data of Guthrie and Bourland[6] and Wucher.[6]

Figure 3 shows χ of liquid Pd-Si alloys as a function of concentration. We observe a drastic decrease of the large paramagnetic χ of pure liquid Pd by adding liquid Si. For the plotted isotherm at 1552°C, χ becomes diamagnetic at concentrations larger than 20 at.% Si. The temperature coefficient of χ^{-1} changes sign from positive to negative at a Si concentration of 10 at.%.

In the following we discuss these results in the light of known theories and calculations.

(i) Pure liquid Si is a simple metal containing only s and p electrons. We split χ into ionic and electronic contributions: $\chi = \chi_I + \chi_e$. Since $\chi_I = -1 \times 10^{-6}$ cm³/g ion[7] we obtain $\chi_e = 13.6 \times 10^{-6}$ cm³/g atom right above T_M. The Pauli-Landau susceptibility for a free-electron system is $\chi_0 = 9.9 \times 10^{-6}$ cm³/g atom if we insert the density of states $N_0(E_F)$ at the Fermi energy appropriate to the four conduction electrons of liquid Si. Dupree and Seymour[3] took into account electron-electron interaction for χ_e, but neglected the electron-ion interaction. They found $\chi_e = 13.6 \times 10^{-6}$ cm³/g atom which is in excellent agreement with our experimental finding. We would like to point out that our result represents the first experimental confirmation of the widely used assumption of four conduction electrons for Si in both liquid and solid amorphous alloys.[8]

(ii) Solid Pd is an outstanding example of an element exhibiting strongly enhanced paramagnetism, described by Stoner theory[9] in terms of

$$\chi(T) = 2\mu_B^2 R(T)/[1 - IR(T)],$$

where I is the effective exchange and the T dependence is determined by an integral over density of states and derivative of the Fermi distribution:

$$R(T) = -\int dE\, N(E)\, df/dE.$$

Our interest lies in the T dependence of χ in order to compare the Stoner-Wohlfarth and the Edwards theories. The measurements show that for $T \gtrsim 800$ K, χ^{-1} is linear in T. This is also true above T_M, but with a smaller temperature coefficient than in the solid. It is therefore tempting to interpret χ in terms of a Curie-Weiss law.

It is a matter of debate whether such a Curie-Weiss law can be expected from Stoner-Wohlfarth theory for $T \gtrsim 800$ K. A linear T dependence of χ^{-1} results for $T > T_F \equiv E_F/k_B$,[10] which is several thousand degrees for metals. Wohlfarth[11] argues that $N(E)$ characteristic of d band can yield $\chi^{-1} \propto T$ for $T \geqslant T_d$, an effective degeneracy temperature much lower than T_F. Lipton and Jacobs[12] estimate $T_d \approx 800$ K for Pd, which agrees quite well with the experimental finding. Moreover van Dam and Andersen[13] evaluated χ for Pd for $T \leqslant 300$ K with $N(E)$ from band structure calculations; the T dependence of their χ is in good agreement with experiment. More recently[14] they extended their calculations to $T \approx 800$ K reproducing very accurately the χ^{-1} curve up to these high temperatures. For higher T, lattice expansion and the T dependence of I would have to be taken into account.

On the other hand Edwards[15] proposed a model for the magnetic properties of fcc metals like Ni, Pd, etc. The nearly filled d band consists of three sub-bands built up by xy-, xz-, and yz-

type d orbitals. Within sub-bands, spins behave like a two-dimensional Heisenberg antiferromagnet with local spin alignment, which explains the relatively well-defined spin waves in Ni above T_c. A mean-field treatment of the coupling between sub-bands yields

$$\chi^{-1}(T) = \chi_{2D}^{-1}(T) + \text{const}.$$

The susceptibility of a 2D sub-band, χ_{2D}, shows Curie-Weiss behavior for $T \geqslant 2T^*$, where T^* is a spin fluctuation temperature of the order of a few hundred kelvins for Pd,[15] which would again be consistent with the straight line for χ^{-1} above 800 K. Though appealing for cubic symmetry, this sub-band model seems much less appropriate for the liquid, which, however, still exhibits Curie-Weiss behavior according to Fig. 2.

The changes in susceptibility ($\Delta\chi$) and its T derivative $[\Delta\chi_T \equiv \Delta(d\chi^{-1}/dT)]$ at the melting point are small (and of the same order as in Co or Ni), so that the same theoretical model should be able to describe the observations in both the liquid and solid states. Briane[16] evaluated $\Delta\chi$ and $\Delta\chi_T$ for Ni-Fe alloys according to a procedure by Adachi and Aisaka[17] who obtained $N(E)$ for the liquid by smoothing the curve calculated for the solid. Briane[16] finds good agreement with experiment for $\Delta\chi_T$, but less good for $\Delta\chi$ itself. It seems possible to explain $\Delta\chi_T$ also for Pd, thus demonstrating that Stoner theory is able to account for χ for solid *and* liquid Pd.

(iii) $\mathrm{Pd}_x\mathrm{Si}_{1-x}$ alloys (Fig. 3) can be understood qualitatively by Stoner theory by taking into account the true density of states and the effective exchange of the Pd d electrons in the alloy. Both quantities are not yet known for the liquid state. Since it is very hard to measure density-of-states data in the liquid state at high temperatures, we take advantage of the empirical similarity between glassy and liquid metals and use density-of-states curves obtained by photoemission measurements on Pd-Si metallic glasses. The glassy samples were prepared by rapid quenching from the liquid state using a novel piston and anvil apparatus operating in high vacuum up to 10^{-8} Torr. Levitation melting was used in order to avoid any possible reaction between the liquid droplet and the crucible material. Careful photoemission[18] measurements using different wavelengths from He I, He II, and x-ray sources yield the following results: The density of states at E_F in the glassy $\mathrm{Pd}_{81}\mathrm{Si}_{19}$ alloy is reduced compared to pure Pd, but still a factor of 3 larger than for s,p states in monovalent noble metals. The resulting shoulder on the high-energy side of the d band in the alloys still has d character. This finding is in good agreement with theoretical band-structure calculations of crystalline Pd,[19] where E_F lies 0.35 eV below the upper d-band edge and a shoulder of empty, high-lying d states is indicated.

Thus, the drastic decrease of the large paramagnetic χ of pure liquid Pd on alloying with Si can be associated with the shift of E_F towards regions of lower density of states. Now the question arises as to whether the minimum of χ around 35 at.% Si is related to a further shift of E_F into a s,p density of states as is known for monovalent noble metals. These diamagnetic susceptibility values are characteristic of the monovalent noble metals in the liquid state.[20] On the other hand, it remains a question why a d-electron density of states at E_F, albeit a very small one, can show diamagnetism.

In summary, we have shown that the magnetic susceptibility of Si changes at T_M from diamagnetic to paramagnetic values. These values are in excellent agreement with theoretical calculations for the liquid state. The magnetic susceptibility of liquid Pd and Pd-Si alloys was measured for the first time. Calculations for these melts are not yet available. Our interpretation favors the Stoner-Wohlfarth theory.

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Infrared Absorption by Elementary Excitations of the One-Dimensional *XY* System

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Far-infrared absorption experiments on PrCl$_3$ at low temperatures show a broad temperature-dependent absorption peaked at 3.0 cm^{-1} which we attribute to cooperative spin excitations. PrCl$_3$ is a one-dimensional *XY* system and a calculation of the mean energy of zero–wave-vector excitations for this model has been carried out. Both the calculated mean energy and the peak of the absorption occur at $1.5J$, where J is the nearest-neighbor interaction parameter.

Praseodymium chloride (PrCl$_3$) and some analogous materials have been of recent interest in that they exhibit a cooperative Jahn-Teller transition with several unusual features.[1] This transition is brought about by an effective electric dipole-dipole interaction between nearest-neighbor praseodymium ions when the ions are in their non-Kramers doublet ground state ($T \lesssim 20$ K). In an $S=\frac{1}{2}$ representation the Hamiltonian for the ion in external magnetic and electric fields can be written as

$$H_l = g_z \beta H_z S_z{}^l + \gamma(E_x S_x{}^l + E_y S_y{}^l) + \sum\nolimits_m J_{lm}(S_x{}^l S_x{}^m + S_y{}^l S_y{}^m), \qquad (1)$$

where the summation is over the nearest-neighbor ions. The crystal structure of PrCl$_3$ and its isomorphs ($C_{6h}{}^2$ symmetry) is such that the nearest-neighbor Pr ions are along the c axis. The dominance of the nearest-neighbor interaction leads to one-dimensional (1-D) behavior to temperatures well below J_{lm}/k_B.[2-4] This has been demonstrated in fits of the specific heat and electric susceptibility measurements by 1-D *XY*-model calculations. These fits enable both the electric dipole moment γ and the pair interaction energy J_{lm} (hereafter written as J) to be determined. Of further interest is the fact that possible indirect evidence for elementary excitations of the 1-D *XY* system was obtained from the thermal conductivity of praseodymium ethyl sulfate (PrEtSO$_4$) and PrCl$_3$.[4] It was the purpose of this present work to obtain more direct evidence for the elementary excitations by using far-infrared spectroscopy coupled with an estimate for the mean energy of zero–wave-vector excitations.

The far-infrared spectrometer has been described previously,[5,6] as also have the cryostats used to maintain the sample at a temperature within the range of 0.4 to 40 K.[7,8] The sample of PrCl$_3$ was grown in Dr. E. H. Carlson's laboratory at Michigan State University by distillation of anhydrous PrCl$_3$ under vacuum, followed by lowering through a gradient furnace. It was mounted with its c axis normal to the axis of the infrared beam so that by means of a polarizer the E field of the beam could be either parallel or perpendicular to the crystalline c axis. The Fourier-transform spectrometer measured the intensity transmitted through the crystal as a function