Superconductors with Magnetic Impurities in a Singlet Ground State

by **E. Bucher, K. Andres, J. P. Maita** and **G. W. Hull, Jr.**
Bell Telephone Laboratories, Inc., Murray Hill, N. J., USA

(6. V. 68)

Abstract. The effect of Pr and Tm doping on the superconductivity of Th and of La-compounds having the Cu_3Au structure is investigated. Although strongly paramagnetic, these alloys remain superconducting to high Pr and Tm concentrations due to the effect of crystal field splitting which produces a nonmagnetic, singlet ground state. The drop in the superconducting transition temperature is compared with the low temperature van Vleck susceptibility and the crystal field splitting as derived from the Stark-type specific heat anomaly. Magnetic properties are also studied in the Th-Pr (fcc) system up to 90 a/o Pr.

I. Introduction

In the last decade, magnetic impurities in superconductors have been studied very extensively and the results have been used quite successfully to learn about the interaction strength of conduction electrons with localized spins [1, 2]. We wish to present here experimental results about a similar problem not previously investigated: the study of superconductors with magnetic ions undergoing a Stark splitting and exhibiting a nonmagnetic ground state characterized by $\langle J_z \rangle = 0$ [3]. In this way we hope to obtain more information about the influence of higher magnetic levels of the impurities and also about the physical nature of exchange forces as one goes toward a critical ratio of exchange energy to crystal field splitting. We confine our study to Pr^{3+} and Tm^{3+} in superconductors of cubic symmetry since non Kramers rare-earth ions are expected to exhibit a nonmagnetic ground state in a field of cubic symmetry. Also Pr^{3+} and Tm^{3+} are the non Kramers rare-earth ions with the smallest spin quantum number ($S = 1$) which should lead to reduced indirect exchange [4]. The basic superconductors are listed in Table 1, including some of their thermodynamic properties. Unfortunately, the most frequently occurring La-compounds of cubic structure (NaCl, CsCl) are not superconducting above 1 °K. The Cu_3Au structure was the only choice left, as well as Thorium metal, in which large fractions of Pr [5] (up to 90 a/o) and Tm (at least 30 a/o) can be dissolved.

II. Experimental

The rare earths used were of standard purity (99.9%). Thorium was of higher purity (99.99%) grown by the iodide process. The Th-alloys and the rare earth-tin and -indium compounds were melted in an arc furnace. The rare earth-Pb and -Tl compounds were reacted in sealed tantalum crucibles. In the ternary systems the rare-earth alloys were first homogenized in an arc furnace. In the Tm-alloys, the final

composition was calculated from the final weight because of the high Tm vapor pressure. The susceptibilities were measured with a pendulum magnetometer [6] and the specific heats with a heat pulse method [7].

III. Results and Discussion

In Table 1, we list the thermodynamic properties of the basic superconductors used for the study. These compounds were simultaneously investigated by GAMBINO et al. [8].

Table 1

Thermodynamic and magnetic data of basic superconductors chosen for doping with Pr and Tm.

Compound	T_c (°K)	$\gamma^*\left(\frac{m\,J}{°K^2\ \text{mole}}\right)$	$\theta_D^*(0)$ (°K)	$\frac{C_{es}}{\gamma\,T_c}$	χ_m^* ($T = 298$ °K) $\frac{\text{cm}^3}{\text{mole}}$
$LaSn_3$	6.55	2.74	205	2.80	
$LaPb_3$	4.07	3.25	147	2.73	11.6
$LaTl_3$	1.51	3.35	144		7.8_5
$LaIn_3$	0.71	1.93	232		

* Calculated for 1/4 of a formula unit.

Figure 1 shows the transition temperature T_c of the 6 systems studied. The depression of T_c in the 5 systems $Th_{1-x}Pr_x$, $Th_{1-x}Tm_x$, $La_{1-x}Pr_xTl_3$, $La_{1-x}Pr_xPb_3$ and $La_{1-x}Tm_xSn_3$ per unit of Pr or Tm concentration is much smaller than in $La_{1-x}Pr_xSn_3$. This is consistent with the low temperature magnetic properties which indicate a temperature-independent van Vleck paramagnetism and therefore a nonmagnetic singlet ground state in the first 5 systems. In $La_{1-x}Pr_xSn_3$ however we found that Pr shows a local moment. $PrSn_3$ becomes antiferromagnetic at 8.5 °K [10] while $PrPb_3$ and $PrTl_3$ are van Vleck paramagnets with susceptibilities of 0.076_0 and 0.096_2 cm³/mole Pr at 1.43 °K.

Figure 2 shows the inverse susceptibilities of $La_{1-x}Pr_xPb_3$ and $La_{1-x}Pr_xTl_3$ as functions of temperatures.

In Figure 3 we also show the low temperature behavior of $1/\chi_m$ vs. T of various Th-Pr (fcc) alloys. We shall discuss the magnetic properties of this system later. In investigating the new superconducting systems we were mainly interested in attempting to establish a relationship between the rate of change of transition temperature dT_c/dx and crystal field parameters (e.g. the splitting Δ between the ground state and the first magnetic level) or, better, the ratio between exchange forces and crystal field splittings. One has to expect a certain minimum critical ratio of these quantities where ordering starts to occur at $T = 0$ [11]. At least a few qualitative conclusions may be drawn at present. From Figure 2 we conclude that Δ is smaller in $La_{1-x}Pr_xPb_3$ than in $La_{1-x}Pr_xTl_3$. In the latter the susceptibility χ_m ($T = 0$) per mole of Pr is independent of x while in the former there is a considerable variation from $\chi_m = 0.19_8$ cm³/mole Pr for $x = 0.1$ dropping to 0.076_0 cm³/mole Pr for $x = 1.0$. In Figure 4 we show the specific heat of

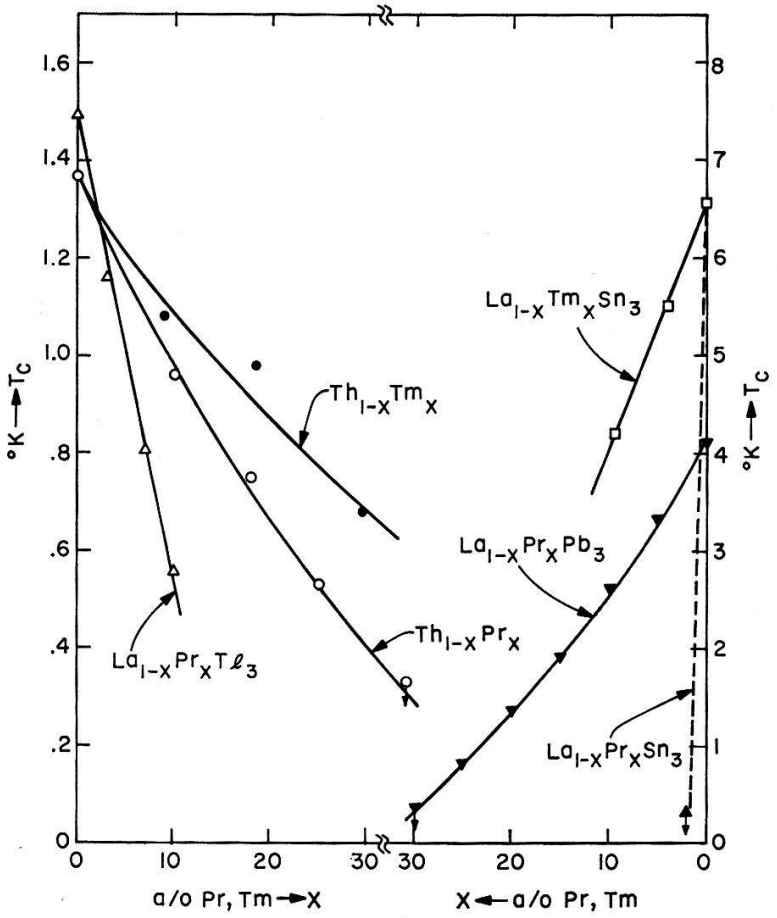

Figure 1

Superconducting transition temperatures of various superconductors doped with Pr and Tm, as a function of Pr and Tm concentration. (Note break in the middle of scale to avoid overlapping.)

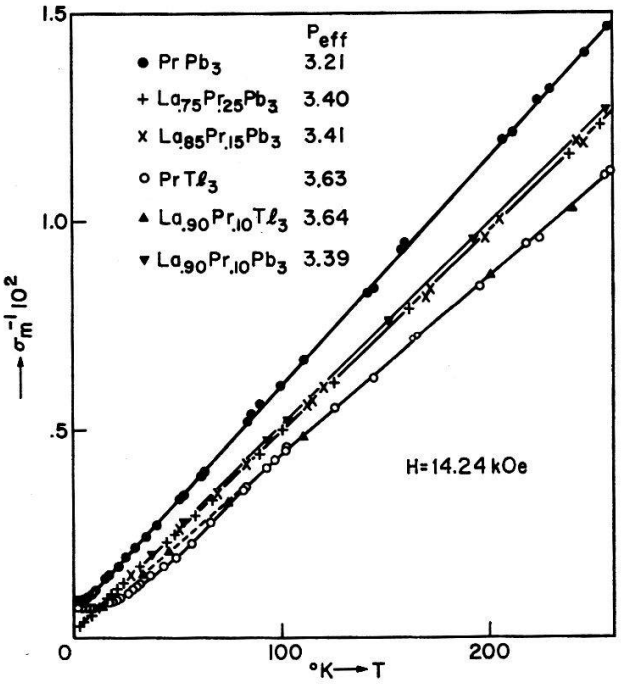

Figure 2

$10^2/\sigma_m$ vs. temperature, σ_m is the magnetization per mole of Pr at $H = 14.24$ kθe (background susceptibility of $LaTl_3$ and $LaPb_3$ subtracted, see Table 1).

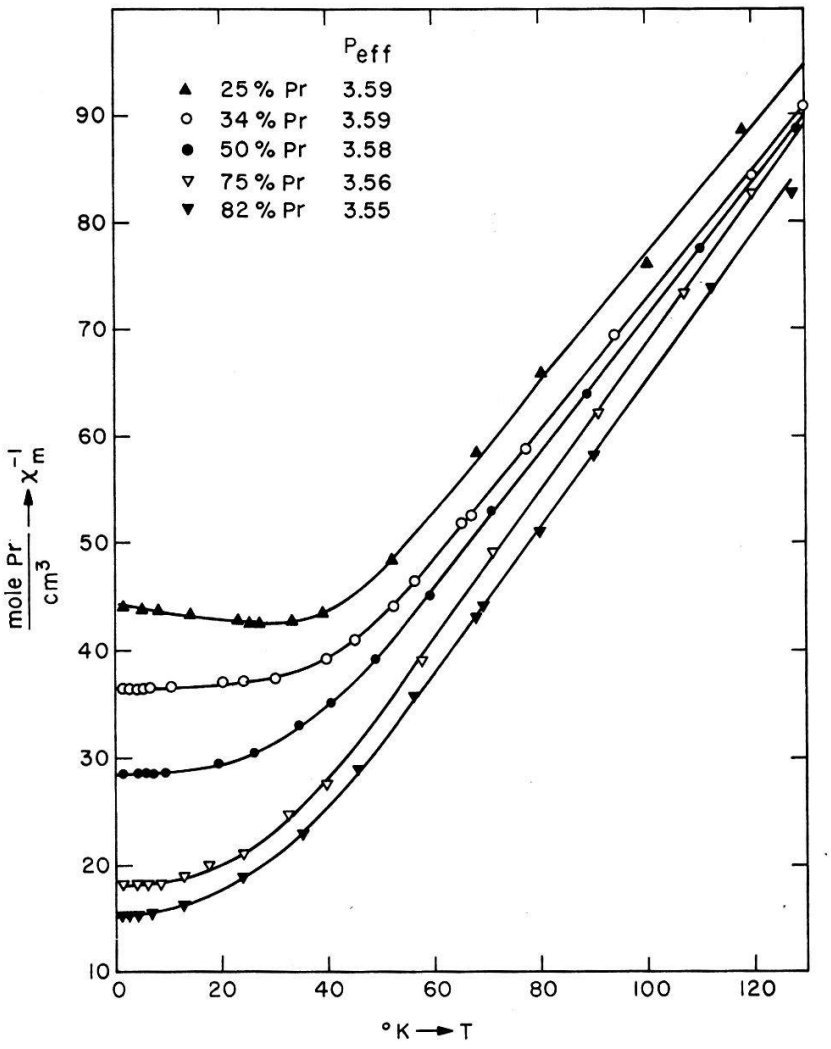

Figure 3

$1/\chi_m$ vs. temperature, χ_m is the susceptibility per mole of Pr.

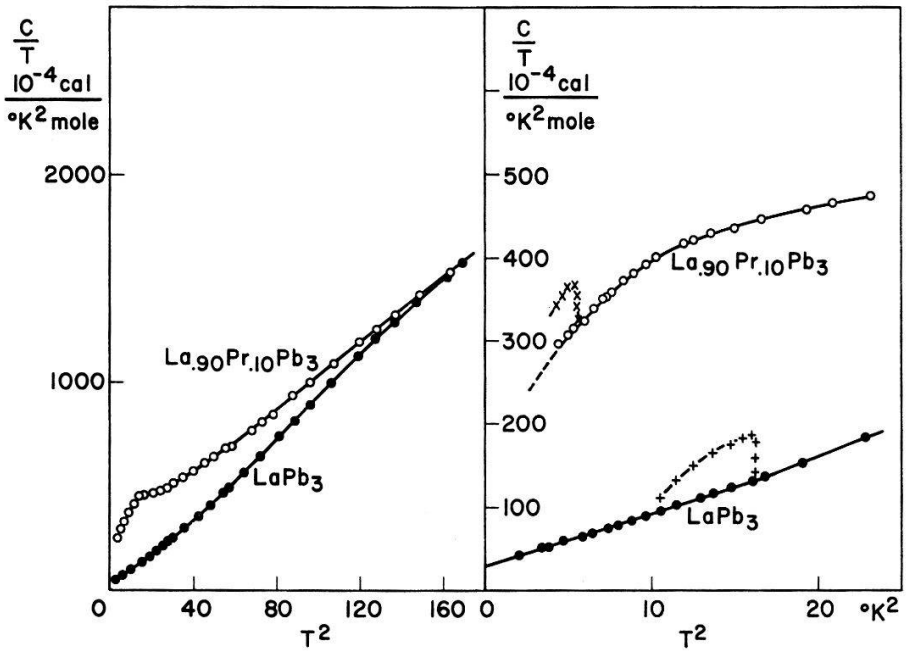

Figure 4

C/T vs. T^2 of $LaPb_3$ and $La_{.90}Pr_{.10}Pb_3$ (C is the specific heat per formula unit).

$LaPb_3$ and $La_{.90}Pr_{.10}Pb_3$. We first note the existence of a bulk transition at 2.65 °K. The specific heat jump $(\Delta C/\gamma T)_{T=T_c}$ is not reduced compared to $LaPb_3$, suggesting that there are no local spins present, responsible for the drop in T_c. In Figure 5 we plot the excess specific heat C_s vs. T of $La_{.90}Pr_{.10}Pb_3$ and $La_{.90}Pr_{.10}Tl_3$ with respect to $LaPb_3$ and $LaTl_3$ respectively and identify these as Stark type specific heat anomalies. It is implicitly assumed that substitution of La by Pr does not change the electronic specific heat, the Debye temperature or its variation with respect to temperature. For $La_{.90}Pr_{.10}Tl_3$ and $LaTl_3$ we can give a proof of the first two assumptions (see Fig. 5, insert). Support for the third assumption is that we get correct values for the specific heat maxima as calculated theoretically. Besides we do not expect an appreciable influence of the low lying 4 f levels on properties depending on the outer shell. The level system of Pr^{3+} $(J = 4)$ in octahedral and cubic symmetries has been discussed by LEA et al. [12]. The splitting pattern should be expected to be the same in the present case the only difference in the Cu_3Au structure being that there are 12 nearest (nonmagnetic) neighbors at the corners of a truncated octahedron. From the specific heat anomalies, we find splitting energies of 18 °K for $La_{.90}Pr_{.10}Pb_3$ and about 37° for $La_{.90}Pr_{.10}Tl_3$. It must be emphasized, that the specific heat anomalies cannot be explained by taking 4th order crystal potential terms only. This would lead to one single maximum of C_s for $\Delta/T = 2.58$, not consistent with Figure 5. Besides the height

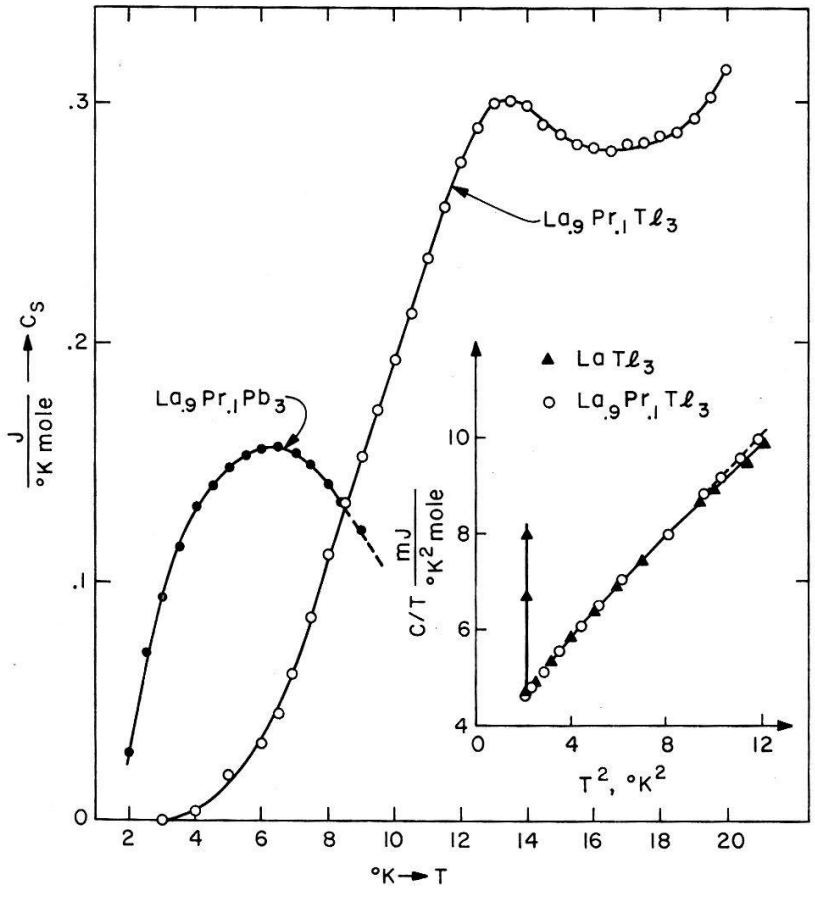

Figure 5

Plot of $C_s = C_{La_{.90}Pr_{.10}Pb_3} - C_{LaPb_3}$ and $C_{La_{.90}Pr_{.10}Tl_3} - C_{LaTl_3}$ for 1/4 of a formula unit vs. temperature, T.

Insert: C/T vs. T^2 of $LaTl_3$ and $La_{.90}Pr_{.10}Tl_3$ also for 1/4 of a formula unit at lowest temperatures.

of the excess specific heat in $La_{.90}Pr_{.10}Pb_3$ is consistent within 1% with the first level being a doublet, rather than a triplet; all other levels being much higher. However the exchange forces may invert the sequence of the higher levels as calculated by symmetry considerations in the work of LEA et al. [12]. Their work is based on the assumption of a point-charge model which might not be applicable in our case, although it explains the crystal field splitting effects in Pr-Va and Tm-Va NaCl compounds very well [13]. In $La_{.90}Pr_{.10}Tl_3$ the structure of the specific heat anomaly can be explained by mixing in 6th order crystal potential terms. It is tempting to ascribe the drop in T_c to the fraction of thermally excited magnetic ions, an idea which is further supported by the flattening out of the T_c vs. x curves at higher Pr and Tm concentration. If t denotes the drop in T_c per unit of concentration of *magnetic* ions one would expect an initial slope of

$$\frac{dT_c}{dx} = t\, e^{-(\Delta/kT_c)} \tag{1}$$

where Δ was defined above and T_c is the transition temperature of the undoped superconductor. t may be estimated from $La_{1-x}Pr_xSn_3$ ($\approx 10°$ (a/o)$^{-1}$), in which indirect exchange forces must be responsible for making the ground state for Pr^{3+} magnetic. Numerical calculations show however, that expression (1) fails completely (especially at higher concentration) in both systems $La_{1-x}Pr_xPb_3$ and $La_{1-x}Pr_xTl_3$. Nevertheless it is interesting to note that $(dT_c/dx)_{x=0}\,\Delta$ is roughly constant in $La_{1-x}Pr_xPb_3$ and $La_{1-x}Pr_xTl_3$. The drop in T_c must be ascribed mainly to the influence of the 4 f shell, although nonmagnetic at low temperatures. This is consistent with the observed intensity of the specific heat peak which would be reduced by the presence of local moments. It is interesting to compare our values with results of MATTHIAS et al. [1] concerning magnetic rare-earth ions in La. Their observed scatter in dT_c/dx vs. the atomic number of the rare-earth ion can very well be explained by crystal field splitting effects. There is evidence that the drop in dT_c/dx for ions with half integral J is always larger than for even J's. In Pr metal e.g. (d hcp structure) there is evidence that the atoms in cubic sites (50%) do not have moments [14, 15], while in hexagonal sites they order antiferromagnetically at 25 °K [15]. In the isomorphous case of La one should expect the same behavior assuming random distribution of the rare-earth impurities and therefore the drop in dT_c/dx may have been underestimated. It would be interesting to determine which type of sites would energetically be preferable for Pr ions in La.

We finally would like to discuss the system Th-Pr, in which the fcc phase persists up to 90 a/o Pr [5]. Figure 3 shows that alloys up to 82 a/o exhibit van Vleck paramagnetism at low temperature, however two samples of 88 and 90 a/o Pr, not plotted in Figure 3, showed a trace of ferromagnetism. Further studies will be necessary to determine whether the alloy system becomes ferromagnetic at a critical concentration before the phase boundary is reached. Another interesting fact evident in Figure 3 is that the exchange interaction changes sign at some concentration, being antiferromagnetic at the Th-rich end, resulting in a sharp increase in the atomic susceptibility towards the Pr-rich end (see also Fig. 6). The alloys with 10 and 25 a/o Pr (Fig. 3) showed a flat susceptibility maximum which is not understood at present. Pure Th did not show anomalous behavior. At low Pr concentrations the Th background susceptibility was subtracted. We found 93.5 cm^3/mole and 92.6 at 298 °K and 84 °K respec-

tively in agreement with SMITH and GREINER [16]. The strong variation of the exchange coupling of course makes it impossible to separate out the crystal-field splitting from a plot of $\log \chi_m(0)$ vs. $\log a$ (see Fig. 6). A point charge model would predict a law of the form

$$\chi_m(0) \sim a^n \tag{2}$$

with $n = 5$ whereas we find from Figure 6 $n = 110$. Nevertheless, the persistence of superconductivity up to 30 a/o Pr at 0.40 °K suggests that the exchange is relatively weak, in agreement with results of PARKS [17] who used Th alloys for adiabatic demagnetization.

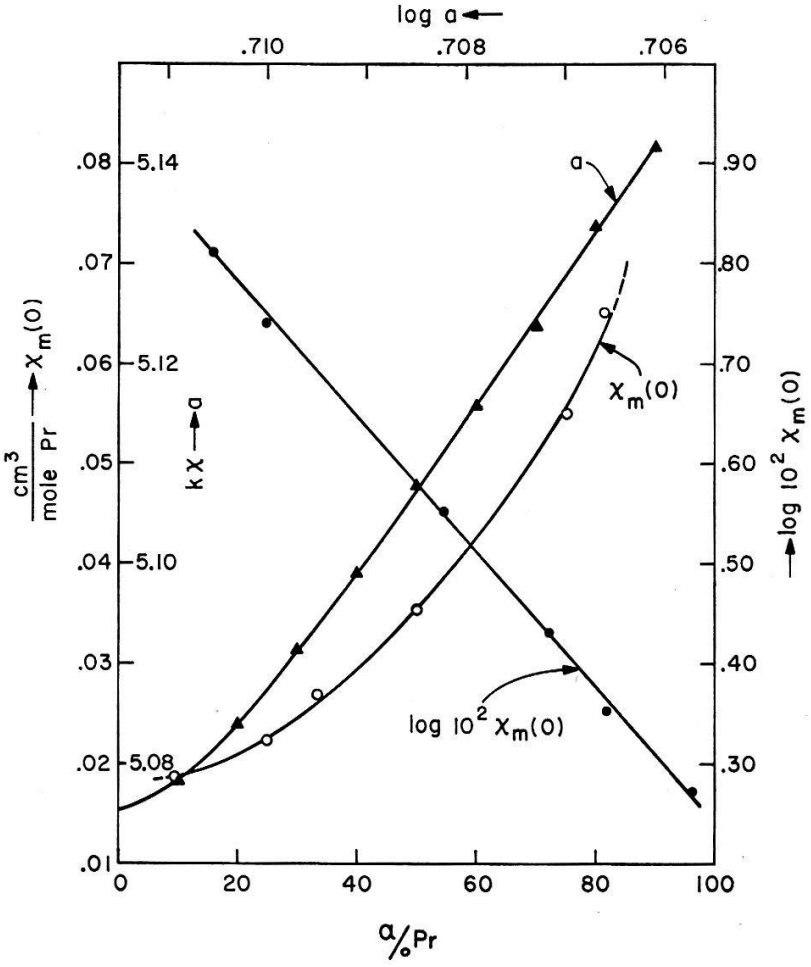

Figure 6

Lattice constants a (from Reference [5]) and low temperature susceptibilities $\chi_m(0)$ (from Figure 3) vs. Pr concentration in Th-Pr (fcc) alloys. A plot of $\log 10^2 \cdot \chi_m(0)$ vs. $\log a$ (right and upper scale) is also included.

Acknowledgment

We are indebted to P. BUSINGER for his help in the numerical analysis. We also have benefitted from discussions with P. W. ANDERSON, D. B. MCWHAN, B. R. COOPER, A. M. TOXEN and especially A. MENTH. We are also grateful for W. M. WALSH, JR. for his critical review of the manuscript and A. S. COOPER for X-ray analysis.

It is a great pleasure to us to dedicate this work to the 60th birthday of Prof G. BUSCH

References

[1] B. T. MATTHIAS, H. SUHL and E. CORENZWIT, Phys. Rev. Lett. *1*, 92 (1958).
[2] P. G. DE GENNES, *Superconductivity of Metals and Alloys* (W. A. Benjamin Inc., N.Y. 1966), Chapter 8.
[3] Part of this work was presented at the Berkeley meeting of the APS, see Bull. Am. Phys. Soc. *13*/3, 427 (1968).
[4] P. G. DE GENNES, Compt. Rend. *247*, 1836 (1958).
[5] M. NORMAN, I. R. HARRIS and G. V. RAYNOR, J. Less-Common Metals *11*, 395 (1966).
[6] R. M. BOZORTH, H. J. WILLIAMS and D. E. WALSH, Phys. Rev. *103*, 572 (1956).
[7] F. J. MORIN, J. P. MAITA, Phys. Rev. *129*, 1115 (1963).
[8] R. J. GAMBINO, N. R. STEMPLE and A. M. TOXEN, J. Phys. Chem. Solids *29*, 295 (1968).
[9] J. E. GORDON, H. MONTGOMERY, R. J. NOER, G. R. PICKETT and R. TOBÓN, Phys. Rev. *152*, 432 (1966).
[10] In agreement with T. TSUCHIDA and W. E. WALLACE, J. Chem. Phys. *43*, 3811 (1965).
[11] B. R. COOPER, Phys. Rev. *163*, 444 (1967).
[12] K. R. LEA, M. J. M. LEASK and W. P. WOLF, J. Phys. Chem. Solids *23*, 1381 (1962).
[13] See e.g. G. BUSCH, J. appl. Phys. *38*, 1386 (1967) and references thereof.
[14] H. NAGASAWA and T. SUGAWARA, J. Phys. Soc. Japan *23*, 701 (1967).
[15] W. C. KOEHLER, J. appl. Phys. *36*, 1078 (1965).
[16] J. F. SMITH and J. D. GREINER, Phys. Rev. *115*, 884 (1959).
[17] R. D. PARKS, Proc. 8th Int. Conf. Low Temp. Phys. (London 1962), Butterworth 1963.

Electric Field Induced Infrared Absorption and Raman Scattering by Optical Phonons in Centrosymmetric Crystals

by **E. Burstein**[1)2)] and **A. A. Maradudin**[3)]
Physics Department, University of California, Irvine, California

E. Anastassakis[1)] and **A. Pinczuk**[1)]
Physics Department and Laboratory for Research on the Structure of Matter, University of Pennsylvania, Philadelphia, Pennsylvania.

(10. V. 68)

Abstract. An externally applied electric field removes the center of inversion of a centrosymmetric crystal by producing relative displacements of the atoms in the unit cell and by deforming the charge distributions of the atoms. The resulting electrically deformed crystal can exhibit a first order (one phonon) infrared absorption by Raman active normally infrared inactive optical phonons and a first order Raman scattering by infrared active (or inactive) normally Raman inactive optical phonons. A discussion is presented of the nature of the tensor coefficients which determine the strength of the electric field induced first order infrared absorption and Raman scattering by optical phonons. Electric field induced Raman scattering spectra in which the electric field of the incident electromagnetic radiation serves as the 'applied electric field' are also discussed.

[1)] Research supported by the U.S. Army Research Office, Durham and the Office of Naval Research.
[2)] On sabbatical leave from the University of Pennsylvania during the academic year 1967/68.
[3)] Research partially supported by the Air Force Office of Scientific Research, Office of Aerospace Research, U.S. Air Force under AFOSR Grant Number 68-1448.