

can be observed with picosecond light pulses in diamond or in any other crystal with a similar density of states in the acoustic branches. Considerably larger light intensities are required (and experimentally feasible); but saturation of the stimulated Raman scattering limits the phonon density  $N_0$ , and crystal damage restricts the practical light flux.

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## High-Temperature Spin-Fluctuation Resistivity in AlMn

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The resistivity of AlMn alloys of concentrations up to 5% is found to decrease linearly in temperature above 50 K, while at lower temperatures it follows the same  $T^2$  behavior observed at lower concentrations. The linear behavior of  $\rho(T)$  rules out the possibility that AlMn is a Kondo system with  $T_K \approx 500$  K. Possible explanations in terms of localized spin fluctuations are suggested.

The AlMn alloy system can be defined as non-magnetic: It does not, in fact, show either a temperature-dependent magnetic susceptibility or the other characteristic electronic properties (e.g., the Kondo effect or a "giant" thermopower) shown by dilute magnetic alloys. It has, however, been shown that this system, together with AlCr, shows "weak" magnetic behavior in several low-temperature properties. It has been possible, in

particular, to observe a very weak resistivity minimum, followed at low temperatures by a quadratic temperature increase in the resistivity obeying a law of the type

$$\rho(T) = \rho(0)[1 - (T/\theta)^2], \quad (1)$$

where  $\rho(0)$  is the zero-temperature resistivity and  $\theta$  a characteristic temperature whose value was found to be  $530 \pm 30$  K.<sup>1</sup>

These results were interpreted<sup>1,2</sup> as due to the presence of localized spin fluctuations (LSF's) in the nearly magnetic virtual bound states (vbs's) formed on the Mn impurities; this interpretation has, successively, been found to apply to results on specific heat,<sup>3</sup> superconductivity,<sup>4</sup> and NMR.<sup>5,6</sup> The question immediately arose, however,<sup>2</sup> whether at high temperatures, i.e., at  $T \sim \theta$ , such a system would behave as a "proper" magnetic alloy displaying, for example, a Kondo effect with  $T_K \sim \theta$ , as suggested by the analysis of the residual resistivity of Al-transition-metal alloys made by Schrieffer<sup>7</sup> and also by some experimental results on atomic form factors by neutron scattering experiments.<sup>8</sup> The possibility is also particularly appealing because in most Kondo systems, at  $T \ll T_K$ , a  $T^2$  dependence has indeed been observed subsequently.<sup>9,10</sup>

Unfortunately, the low solubility of Mn in Al, and the predominant contribution of nonmagnetic deviations from Matthiessen's rule,<sup>11,12</sup> have until now allowed only a qualitative estimate<sup>11</sup> of the LSF resistivity at  $T \sim \theta$ ; and the same difficulty has arisen in the few other systems<sup>13</sup> which show similar behavior. We present here the first experimental data on the LSF resistivity of AlMn from liquid-helium temperatures up to above 500 K. They have been obtained on super-saturated alloy samples of concentration between 2 and 5 at.%, which have been prepared by ultra-rapid quenching of the molten alloy in a newly developed mill device.<sup>14</sup> Samples of this kind have recently been investigated in their residual resistivity,<sup>15</sup> superconductivity,<sup>16</sup> and thermoelectric power,<sup>17</sup> and have been found to obey very closely the low-temperature behavior observed in more dilute alloys.<sup>18-20</sup> Moreover, very accurate measurements now in progress on AlMn and AlCr show<sup>21</sup> that their low-temperature resistivity displays a concentration-independent  $T^2$  behavior with a  $\theta$  in agreement with the value quoted above.<sup>1</sup>

In Fig. 1 are shown experimental results of the resistivity measured as a function of  $T$ . The measuring accuracy for  $R(T)$  was  $1/10^4$ ; the technique employed has been described in Ref. 15. The accuracy in determining the absolute values of  $\rho$  is limited to 20% by the difficulty in evaluating the size factor (the commonly used residual resistivity ratio is of no use, the resistance minimum being well above room temperature).

By means of very high-accuracy measurements down to lower temperatures and concentrations,<sup>21</sup> the low-temperature part of the curves has been

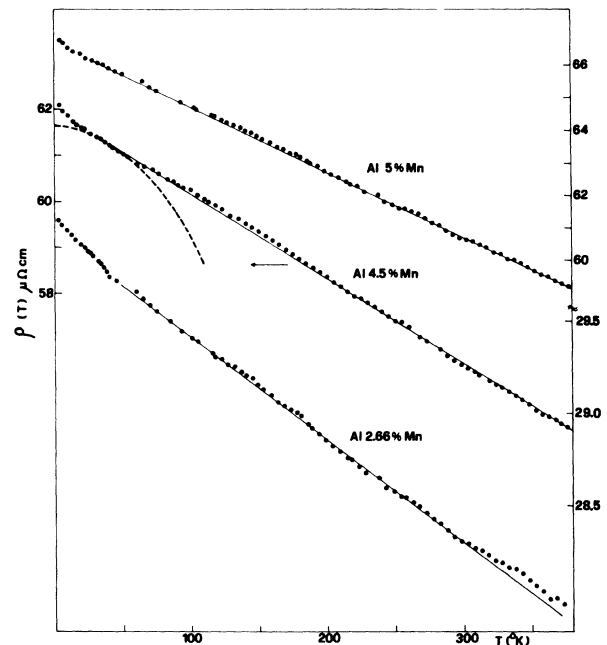


FIG. 1. Resistivity of AlMn as a function of temperature for three representative samples. For the sample with  $c = 4.5$  at. % Mn, the dashed line indicates the  $T^2$  dependence  $\rho(T) = \rho(0)[1 - (T/\theta)^2]$ , with  $\theta = 500$  K; the low-temperature increase above the  $T^2$  law is spurious and has been found not to influence significantly the resistivity behavior about 40 K.

explained as the overlap between a low-temperature spurious dependence, due possibly to more nearly magnetic pairs and clusters of Mn atoms, and the  $T^2$  dependence observed at lower concentrations (a similar condition has already been observed also in other systems.<sup>9</sup> The  $T^2$  behavior has been plotted in Fig. 1 for the sample with  $c = 4.5$  at. % with the curve given by formula (1), using  $\theta = 500$  K. It is quite clear that the  $T^2$  dependence extends up to 45–50 K, but that above this temperature the dependence of  $\rho(T)$  is linear in  $T$  up to the highest temperature.

The phonon resistivity does not seem to give any contribution to the high-temperature part, and it has not been possible to detect any resistance minimum up to the highest temperatures. Any phonon contribution above room temperature would vary linearly with temperature and would not alter the linear temperature dependence of the impurity resistivity. An evaluation of this contribution is very difficult, the resistivity of our alloys being about one order of magnitude higher than the phonon resistivity in pure Al, and this leads us to consider this contribution as small.

The above results rule out the possibility that  $AlMn$  is a Kondo system with  $\theta = T_K$ ; in this case, in fact, we should observe a nearly  $\ln T$  dependence at least above  $\frac{1}{2}T_K$ ,<sup>10</sup> whereas the observed dependence goes from  $T^2$  to  $T$ . Neither are we in a logarithmic "tail," because this would imply a very high  $T_K$  and would be in contrast with the magnitude of the observed decrease.

We must now see whether such a temperature behavior is explainable in terms of LSF scattering at finite temperatures. Theoretical calculations based on the LSF concept have been published,<sup>22</sup> which yield a  $\ln T$  dependence, but do not seem to apply to our case. However, more recently, Kaiser and Doniach<sup>23</sup> have found a universal curve for spin-fluctuation resistivity when the local enhancement factor is large and temperature independent. They found a resistivity which *increases* as  $T^2$  up to approximately  $0.2T_s$  (where  $T_s$  is the spin-fluctuation temperature) and then linearly with  $T$  above this value. They also suggest that, when LSF's coexist with a strong resonant scattering on the vbs's, then the LSF scattering of the electrons would *decrease* the resistivity by pushing the scattering off resonance (i.e., by decreasing the phase shift from  $\pi/2$  to some lower value).

The above argument would seem to apply to our case; however, we must note that we observe the transition between  $T^2$  and  $T$  behavior at  $T \leq 0.1\theta$ . It is also difficult to evaluate how the above argument explains quantitatively the magnitude of our observed decrease with  $T$ . If, in fact, the resonant scattering [i.e.,  $\rho(0)$ ] is "pushed off resonance" by an amount such as to equalize the LSF scattering we should have a behavior of the type<sup>23</sup>

$$\rho(T) = \rho(0)[1 - \frac{1}{3}\pi^2(T/T_s)^2]$$

at low temperatures, and

$$\rho(T) = \rho(0)(1 - \frac{1}{2}\pi T/T_s) \quad (3)$$

at temperatures above  $0.2T_s$ . Formula (2), which is identical to that derived by Caplin and Rizzuto,<sup>1</sup> compared with the low temperature results would imply  $T_s \approx 900$  K (in better agreement with NMR data<sup>9</sup>), so that the high-temperature linear part should extrapolate to  $\rho(T) = 0$  at  $T \approx 600$  K, while the experimental linear part extrapolates to zero at  $T \approx 3300$  K (the phonon contribution could alter this estimate by some 10%). We have not, however, properly derived formulas (2) and (3) from the original ones, and further theoretical investigation in that direction

seems to be worthwhile also taking into account possible variations of the enhancement factor  $\eta$  which are not, however, detected by susceptibility measurements.<sup>24</sup>

Another possible way to explain the experimental data, following the same approach as that of Ref. 1, consists in taking into account the dynamical splitting between the spin-up and spin-down vbs's induced by the spin fluctuations, by introducing an effective energy width  $\Delta' = \Delta/\eta$  and then using the Sommerfeld expansion to calculate the scattering cross section. By assuming in a first approximation that the effect of the thermal fluctuations can be approximated by considering, in place of one vbs of Lorentzian shape, two such states shifted by  $\pm kT$  around  $E_F$ , we obtain at high temperatures a dependence which follows closely a linear  $T$  dependence<sup>25</sup>; again, however, the model is too crude to be pushed further.

Of interest also will be the extension of any theory to the thermoelectric power measurements on these alloys, which show a linear behavior in  $T$  in the  $T^2$  region of the resistivity, flattening off gradually and becoming  $T$  independent above 100 K.<sup>17</sup>

By relating the above findings with the observations of a  $T^2$  term in the low-temperature resistivity of Kondo alloys ( $T \ll T_K$ ), it seems possible to suggest that, also in these last alloys, this term is indeed caused by thermal fluctuations of the "nonmagnetic" compensated state; in this case, however, the relevant parameter,  $T_{sf}$ , is related to the "binding energy"  $kT_K$ .

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## Surface Electric-Field-Induced Raman Scattering in PbTe and SnTe<sup>†</sup>

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Electric-field-induced scattering by normally Raman-inactive LO phonons is observed in the IV-VI-compound (NaCl structure) semiconductors PbTe and SnTe with Pb films on *p*-type samples to induce energy-band bending. The observed Raman peaks correspond to unscreened  $q \approx 0$  LO phonons. A discussion of the mechanisms contributing to the surface field-induced Raman scattering in these materials is presented.

We have investigated electric-field-induced Raman scattering by LO phonons in the cubic IV-VI-compound semiconductors PbTe and SnTe using metal films to induce surface electric fields via energy-band bending. These semiconductors are centrosymmetric crystals, and furthermore all atoms are at centers of symmetry. Therefore, all  $q = 0$  vibration modes have odd parity and are Raman inactive. Using cleaved *p*-type samples of PbTe and SnTe coated with semitransparent films of Pb, we observed Raman peaks in backscattering corresponding to  $q \approx 0$  LO phonons. Scattering was observed only for parallel polarization (i.e.,  $\hat{e}_i \parallel \hat{e}_s$ , where  $\hat{e}_i$  and  $\hat{e}_s$  are the polarization vectors of the incident and scattered radiation). The observed peaks show resonant enhancement at the  $E_2$  energy gaps. The peaks do not appear in the absence of the Pb films.

It is known that the position of the Fermi level

at the surface of ionic crystals relative to the band edges is not strongly pinned, and that the energy bands can be "bent" by the presence of metal films at the crystal surface.<sup>1</sup> In the specific case of PbTe, Nill *et al.*<sup>2</sup> have shown that Pb and other metals having low work functions produce an inversion layer at the surface of *p*-type crystals. We note, on the basis of their barrier data for Pb on PbTe, that the width of the space-charge region is  $\sim 360 \text{ \AA}$ , and that the electric field within the space-charge region ranges as high as  $10^5 \text{ V/cm}$ . Similar characteristics are expected for SnTe; however, we have no estimate of these parameters since barrier-height data are not as yet available.

The bent bands and the associated electric fields modify the Raman-scattering selection rules by lowering the symmetry of the crystal and its atomic and electronic excitations. In the presence of the surface electric field  $E_A$ , the LO