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Sharp coupling transition of Gd in AlGa solvents*

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We report NMR and susceptibility measurements on liquid AlGa alloys doped with Gd impurities. Results for the AlGa host alloys show that the solvents form an almost ideal isovalent free-electron-like series of alloys. The coupling of Gd 4*f* cores to the conduction band, as revealed by the Al^{27}, Ga^{69}, and Ga^{71} Knight shifts, nevertheless exhibits an abrupt transition from strong coupling in Al-rich hosts to very weak coupling for Ga-rich solutions. This takes place with no marked change in the impurity susceptibility. The transition occurs at 96-at.% Al, and is much sharper than similar transitions previously reported for Gd and Ho in Al–noble-metal liquid hosts. Neither the structure of the strong-coupling configuration nor the mechanism of the transition can as yet be established definitively.

I. INTRODUCTION

Magnetic impurities in insulators can often be understood in relatively simple terms. However, magnetic impurities in metals have presented difficult and puzzling problems that remain only partly resolved at the present time. In insulators, the impurity structure can be viewed as atomic or ionlike with a superposed crystal field or covalent splitting. Interactions among impurities are interpreted through theoretical schemes made familiar by molecular chemistry. In the case of metals however, there remains the ever-present complication of a mobile electron gas, and difficulties associated with the way in which the local-impurity magnetism couples to translational properties of the host band states. While the impurity structure is determined by coarse chemical features that may be largely independent of the host, there exist major features of the host-impurity coupling that are not at present well understood. It is with one aspect of this latter area—an abrupt transition in impurity-host coupling—that the present paper is concerned.

It has been generally agreed that lanthanide (4*f*) impurities in ordinary metallic hosts are in principle simpler to understand than iron-group (3*d*) elements. The reason is that the 4*f* states lie so deep inside the rare-earth core that they are largely decoupled from host band states. The 4*f* shell is viewed as a quasiatomic structure, as in insulators, coupling weakly to the conduction band and thereby surrounding itself with Ruderman-Kittel-Kasuya-Yosida (RKKY)[1] type spin-density oscillations. This model gives a very satisfactory account of the magnetic and other properties of pure rare-earth metals,[2] although the band structures of these substances remain rather poorly understood. In the face of this broad success, circumstances that render the simplifications invalid assume a greater significance.

The present paper reports a study of 4*f*–to–conduction-electron coupling for a situation in which the perturbative viewpoint of weak RKKY coupling manifestly breaks down. Stupian and Flynn[3] found that all rare-earth impurities with unfilled 4*f* shells couple very strongly to the conduction band of the solvent Al. The coupling is two order of magnitude weaker in liquid-noble-metal hosts,[4] as measured by the spin-density disturbance at nuclei in the surrounding lattice, and the strong coupling of Gd emerges rather abruptly at ~50 at.% Al with Al additions to the noble-metal host.[5] Detailed studies of Ho in AlAg liquid hosts show further that the weak and strong couplings are associated with two different configurations of Ho impurities, each thermally populated, that nevertheless each exhibits the effective moment of the spin-orbit-coupled Ho free ion.[6] There is no reason to suppose that the remaining 4*f* ions behave in a way substantially different from that of Gd and Ho, but the measurements are exacting and have not been undertaken. A related transition has been found in solid intermetallic compounds containing rare earths.[7]

An attempt was made in the present work to identify host materials other than Al for which strong-coupling effects could be detected. No alternative pure host metals were found. In order to reduce the coupling transition to its simplest ingredients, we chose to study a system in which valence differences among the constituents were minimized, and the alloy approached, as nearly as possible, the ideal of isolated 4*f* shells in a uniform Fermi liquid. For this purpose, the Al-Ga system was chosen as a uniform host metal with almost equal sized solvent atoms, each trivalent, and therefore isovalent with rare earths. The impurity element Gd was chosen for its ideally simple core structure, containing one exactly filled 4*f* subshell. Both the AlGa host materials and the Gd-doped alloys were investigated in the liquid state, using NMR and bulk susceptibility measurements.

It turned out that the AlGa system provides an almost ideal host of a nearly-free-electron character. In this host, the Gd core coupling to the conduction band is found to undergo a strong-to-weak transition of remarkably small breadth certainly occupying less than 3 at.% of host alloy composition. We presume that this surprising result may be attributed in part to the ideal nature of the solvent. It may be remarked that a price must be paid for the choice of host in the elaborate procedures required to fabricate homogeneous samples. Details of this work, together with the experimental results, will be found in Sec. II below. The results are discussed in Sec. III, but several aspects of the observations remain obscure.

II. EXPERIMENTAL

A. Alloy preparation

Alloys were prepared from high-purity materials in evacuated quartz capsules held at ~1100 °C by an induction furnace that promoted mixing of the melt. The liquids were quenched to preserve macroscopic homogeneity and so ensure that filed samples for NMR studies contained uniform material.

In the case of Ga-based alloys, major difficulties were encountered owing to the low melting point of Ga. Cold water quenches from the melt caused the alloys to react chemically and led to extensive segregation of the samples. A faster, cleaner quench was devised. Cavities were machined in the face of a copper block, and the molten alloys poured into the cavities while the block was held at liquid N_2 temperatures. The quenched alloys were kept cold, even during the filing procedure, in order to prevent segregation. The results of Knight-shift measurements proved to be imperfectly reproducible until these elaborate procedures were perfected. Thereafter, reproducible results were obtained.

B. Experimental methods

In this work, the solvent Knight shift and bulk susceptibility of a variety of liquid alloys were measured in the temperature range (700–1100) °C. Details of the methods employed have been reported elsewhere.[6] Here we present only a brief summary.

Thin-walled Al_2O_3 thimbles were used to isolate the molten alloys from the fused-silica walls of the evacuated capsules used for susceptibility measurements. A region of inhomogeneous field in a 40-kG superconducting solenoid, containing a furnace operating at temperatures up to 1200 °C, provided the field force which was measured by means of a chemical balance. The small diamagnetic contributions of silica and quartz were eliminated by subsidiary measurements, and absolute susceptibilities were obtained by calibration methods discussed by Rigert.[8] These procedures gave alloy susceptibilities generally accurate to 1% or $\pm 0.03\times 10^{-6}$ mole^{-1} for the size of specimen used here.

Knight-shift measurements were made on filed powders dispersed in degased Al_2O_3 powder and enclosed in evacuated fused-silica capsules. In the case of Ga alloys, the material was maintained at liquid N_2 temperatures until filed, to prevent macroscopic segregation, as mentioned in Sec. II A. NMR detection proceeded by conventional methods using an Anderson bridge-cascade preamplifier system feeding an audio amplifier and phase-sensitive detection (PSD) circuits. The PSD output led to voltage-to-pulse converter and signal-averaging equipment. Fractional Knight-shift changes of the Al^{27} resonance signal could be measured in this way to $\sim 2\times 10^{-3}\%$ or ~4 parts in 10^6 of the resonance frequency.

C. Results for pure hosts

It has been established in previous work that rare-earth impurities in liquid Al cause large solvent Knight-shift changes. For this reason we investigated the coupling of Gd impurities to the conduction electrons of several other host metals having large valence bandwidths or large conduction-electron densities in a search for similar effects in other solvents. None were found. In, Ga, and Sb liquid solvents exhibited negligibly small coupling to the $4f$ core states despite a demonstrated solubility of rare-earth elements in the liquid melts. The strong coupling was found to persist for Gd impurities some 40% of the way across the Al-Si system, but the Si-rich end of the range of solutions was inaccessible and the possible existence of strong coupling for rare earths in liquid Si remains unresolved. The detailed results of these investigations are reported by one of us (E.N.K.) elsewhere.[9] It is not yet clear that the strong coupling found in Al-rich alloys will be observed for any alternative host lattices. Further studies reported here therefore pertain to systems containing Al.

D. Results for hosts alloys

The AlGa system chosen as the focus of this work proved to be an almost ideal nearly-free-electron-like solvent. This feature shows up most clearly in the Knight-shift results. The fractional changes in Knight shift of the solvent Al^{27}, Ga^{69}, and Ga^{71} NMR signal are shown as functions of host composition c (atomic percent) in Fig. 1. These results were obtained at an operating temperature of about 713 °C, but the Al^{27} Knight shift, which could be measured most accurately, suffered no further shift, within the experimental uncertainty, when the temperature was raised to 917 °C.

Figure 1 shows that the electronic structure is

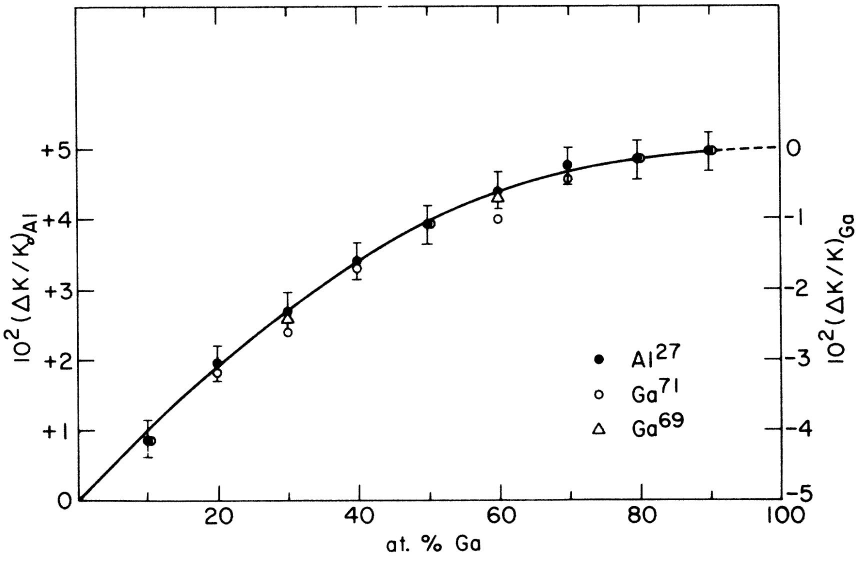

FIG. 1. Al^{27} and Ga (Ga^{69} and Ga^{71}) Knight shifts ΔK in AlGa liquid alloys of various compositions at 713 °C. Note that different zeros are used for Al and Ga fractional resonance shifts, $\Delta K/K$.

not grossly modified by intersolution of Al and Ga in the liquid phase, since the observed Al and Ga solvent Knight shifts vary smoothly and very slowly with composition over the entire range of solutions. When viewed on a fine scale the data confirm this overall view of the solution to a much more detailed extent. Figure 1 shows in addition that the Al and Ga nuclei experience *identical* fractional changes of Knight shift across the entire composition range, within an estimated uncertainty of ~0.1%. Apparently any charge transfer effects, which could cause complementary changes of *s*-electron density at the Al and Ga sites, are almost negligibly small in these alloys. Since the cell structures are expected to be largely *s*- and *p*-like, this indicates that short-range modifications in electronic structure, caused by dissimilarities between the Al and Ga atomic potentials, play no significant role. The observed Knight-shift changes are almost certainly caused by the composition dependence of the spin susceptibility, and take an almost ideal form in which the different nuclear species sample the same electronic structure. It is this manifest electronic homogeneity of the AlGa system that makes it ideal for studies of the coupling transition described in Sec. II E below.

Susceptibility measurements were performed on some AlGa alloys mainly for the purpose of determining the contribution of Gd impurities to the susceptibility of these systems. The bulk susceptibility is dominated by the excess core diamagnetism of the Ga component, and provides little useful insight into the electronic structure of the conduction band. Some results given in Fig. 2 show that the molar susceptibility varies almost linearly with composition from that of pure Al to the value for pure Ga. This is to be expected when the difference between the Al and Ga core susceptibilities is large and independent of composition, and when the electronic susceptibility is insensitive to, and varies smoothly with, the host composition, as indicated by the Knight-shift results. It may be observed that the Ga 3*d* shell at ~ -28 eV lies substantially below the Al band edge. Anomalies connected with the mixing of 3*d* states with the conduc-

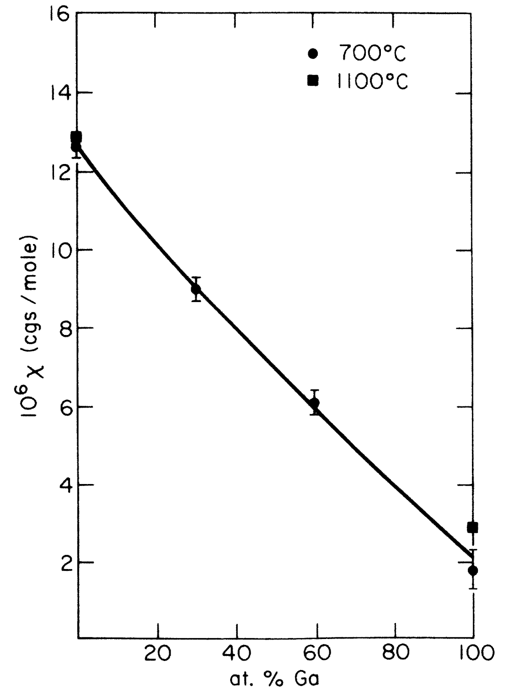

FIG. 2. Susceptibilities of AlGa alloys, mainly at 700 °C.

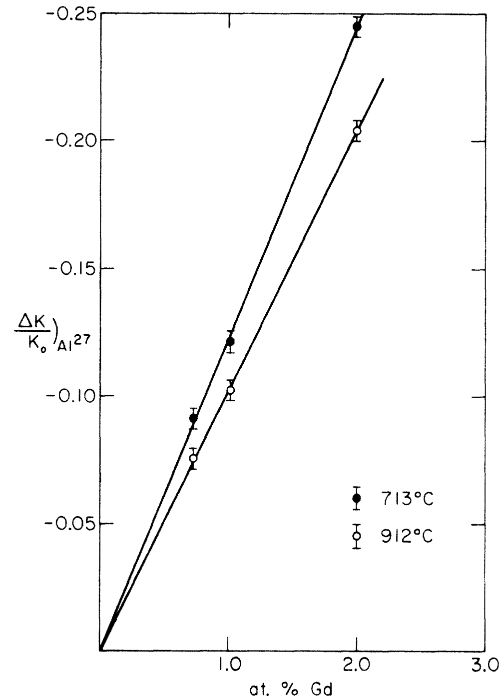

FIG. 3. Shift of the Al^{27} resonance as a function of Gd doping in Al−55-at.%-Ga at two temperatures.

tion band, similar to those associated with Zn in Al, are therefore not expected in the AlGa system containing Gd.

E. Gd impurities in liquid AlGa alloys

Gd impurities cause large temperature-dependent changes of the Knight shift and susceptibility of Al-rich alloys, but only the susceptibility of Ga-rich alloys is strongly modified. It was observed that the NMR linewidth increased with Gd concentration, but was insensitive to host composition. The host nuclei became decoupled from the impurity $4f$ magnetic moments very abruptly as the Ga concentration increased beyond 96 at.%. Figure 3 shows by way of example the Al^{27} fractional Knight shift change $\Delta K/K_0$ caused by small Gd additions to 45-at.%-Al−55-at.%-Ga at 713 °C and 912 °C. Here, K_0 is the Knight shift in pure Al. The shift is linear in Gd concentration, showing that the dilute limit is being probed, and $\Gamma = K_0^{-1}(dK/dc)$ is clearly temperature dependent. The Ga^{71} results for alloys containing 93-at.% and 96-at.% Ga, presented in Fig. 4, clearly demonstrate that the Gd solubility there exceeds 1%.

No comparable effort was made to establish that the impurity susceptibility varied linearly with c since (a) the existence of Gd solubility was determined by the linear dependence of Γ on c and (b) the Gd susceptibility proved to be stable near the free-ion value for all liquid solvents and, indeed, for solid intermetallic compounds also. An investigation of $\chi(c)$ would therefore have served no purpose, and values of the effective magnetic moment were obtained from single specimens for particular host compositions.

Figure 5 shows the effective magnetic moment μ that describes the *excess* magnetism introduced by Gd into various AlGa liquid solvents at 715 °C. These results were obtained by subtracting from the observed susceptibility the relatively small contribution originating in the host lattice, according to the results of Sec. II C. From Fig. 5 we see that the Gd moment remains sensibly constant at the value for pure Gd metal, within the experimental uncertainty of $\sim 0.1\mu_B$, and at a value $\sim 0.2\mu_B$ greater than the theoretical value of $7.94\mu_B$ for free ions. It is possible, but not fully established, that μ falls to slightly smaller values on passing to the pure Ga host.

The Gd-induced Knight-shift changes of Al^{27} solvent nuclei are shown as a function of AlGa host composition in Fig. 6 for an observation temperature of 713 °C. Results taken at higher temperatures fit this trend precisely when scaled by the susceptibility difference between the two temperatures. The value of Γ decreases smoothly and very slowly with increasing Gd content out to ~85-at.% Ga, and thereafter decreases more rapidly. The weak Al^{27} resonance was not studied in alloys containing < 3% Al. However, the variation of the coupling with concentration could be monitored accurately in this region by means of the Ga^{69} and Ga^{71} resonance shifts. These are shown as func-

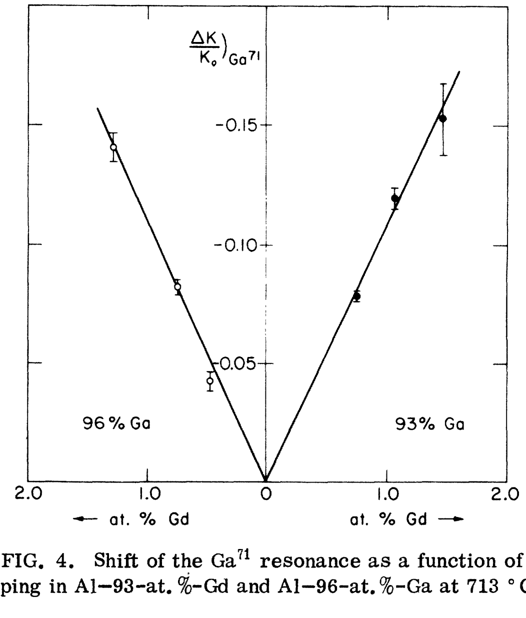

FIG. 4. Shift of the Ga^{71} resonance as a function of Gd doping in Al−93-at.%-Gd and Al−96-at.%-Ga at 713 °C.

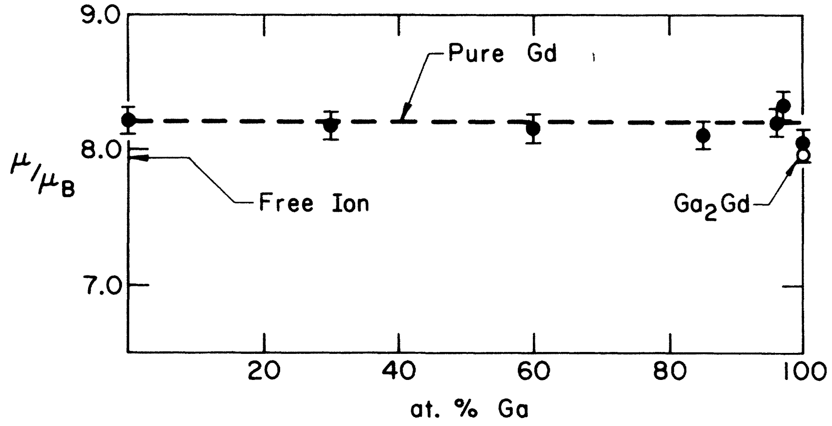

FIG. 5. Effective magnetic moment of Gd ions in various liquid AlGa alloys at 715 °C, compared with the values in pure Gd (broken lines) and $GdGa_2$.

tions of host composition in Fig. 7.

Superposed on Fig. 7 as a broken line is the variation of Γ for Al, multiplied by a factor 1.1. The solid line indicating the trend of the Ga results follows the scaled Al results quite closely, although the Ga data contain more scatter originating from the larger Ga resonance linewidth. When thus scaled, the values of Γ for Al and Ga follow a common variation with host composition to an accuracy of ~10%. Evidently the similar properties of the two distinct host species, exhibited in Sec. II C above, persist also in their response to the Gd core coupling with the conduction band.

In addition, the Ga data reveal the behavior of Γ in the Ga-rich region for which the Ga concentration exceeds 96 at.%. The Ga^{69} and Ga^{71} Knight-shift changes fall abruptly to zero, within experimental uncertainty, from a value of about $\Gamma \sim -10$ immediately before the transition. The coupling decreases by two orders of magnitude. The Al and Ga shifts show very similar decreases over the interval between 85-at.% and 96-at.% Ga, and we therefore suppose that the Al shift also undergoes a sharp modification at ~96-at.% composition, although this has not been verified.

The transition is so sharp that ordinary methods of alloy preparation are not entirely satisfactory. To investigate in greater detail the precise form of the transition, a single alloy was cycled through the transition by remelting with small additions of Al or Ga. The resulting data are shown in Fig. 8. A strongly shifted line of weak intensity was observed in the initial 97-at.% Ga alloy, together with an intense unshifted line. Al additions changing the concentration to 96-at.% Ga modified the NMR spectrum to a single strongly shifted line. Successive Ga additions to give concentrations of 96.5-, 97.0-, and 97.5-at.% Ga restored the resonance to a single unshifted line, as indicated in Fig. 8. Two lines with typical intensity ratios ~4:1 were observed at the intermediate compositions. We believe that the emergence of the double line may

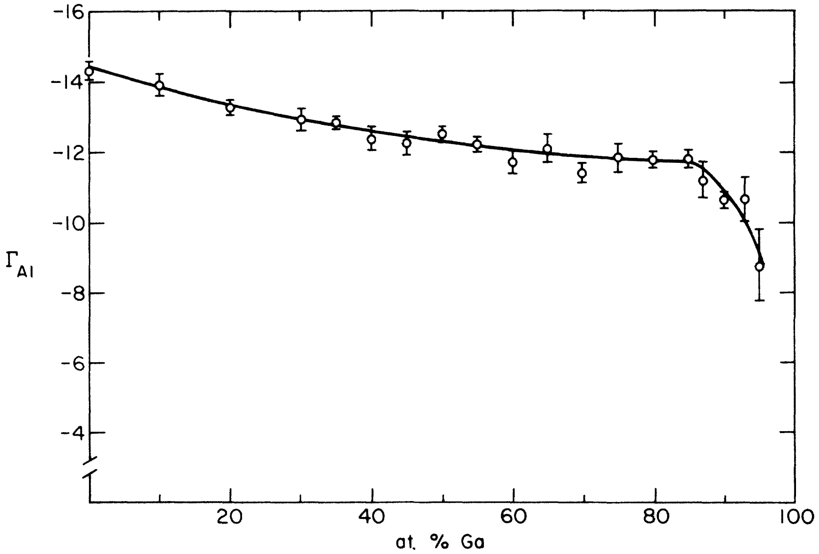

FIG. 6. Al^{27} resonance shift. $\Gamma_{Al} = K^{-1}(\partial K/\partial C)$ caused by Gd additions in various liquid AlGa alloys at 713 °C.

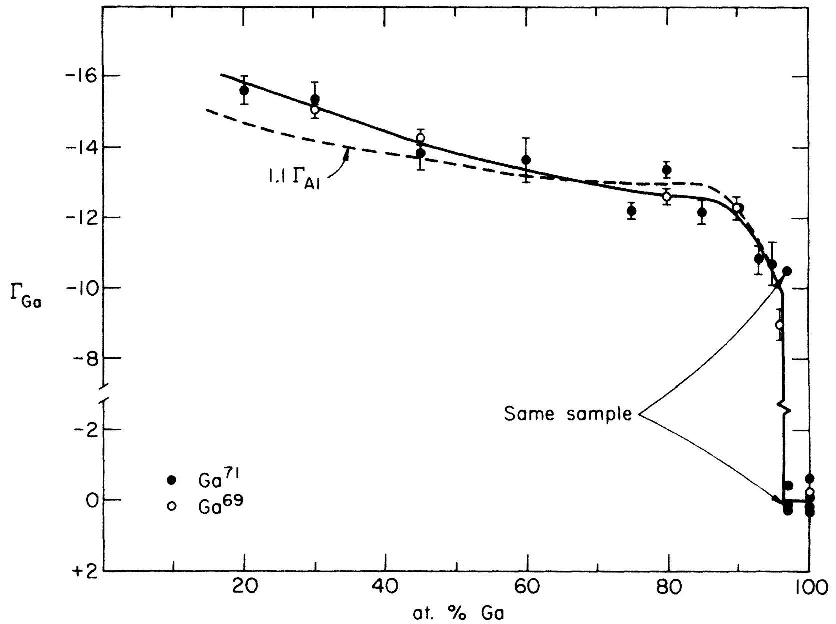

FIG. 7. Ga resonance shift $\Gamma_{Gd}=K^{-1}(\partial K/\partial C)$ caused by Gd additions in various liquid AlGa alloys at 713 °C. The broken line indicates the trend shown for the Al resonance in Fig. 7, scaled by a factor 1.1.

be associated with small residual inhomogeneities in the sample. Even so, the full width of the coupling transition, as observed, occupies only ~1 at.% in composition, and the width for fully homogeneous alloys may be substantially less. On the other hand, the apparent transition may be sharpened by solubility effects.

A considerable effort was made to establish that the coupling transition was not caused by a lack of Gd solubility in Ga. The effort was spent, for the most part, to no avail as no marked Gd-induced shift of the Ga resonance could be detected. The point is that the alloys are homovalent, and even scattering caused by valence structural differences among the components is undetectable for concentrations ~1 at.%, although these differences proved adequate for earlier studies of rare earths in noble metals. However, it was observed that Gd additions caused mechanical modifications to the Ga host, so that the existence of some solubility was in fact established. In addition, the sharpness of the transition in tne face of solubilities determined by Knight-shift methods for the range 90–95-at.% Ga make any explanation of the decoupling transition in terms of solubility very difficult.

Recently, however, this point has been settled beyond doubt by published direct studies[10] of the solubility of Gd and other rare earths in Ga by electrochemical methods. The solubility >0.5 at.% for Gd in Ga at $T>700$ °C is amply big enough to cause large shifts for moderately large coupling. Therefore, the existence of the coupling transition is established. In the absence of known solubilities in the alloy solvents, some residual question remains about the width of the transition. In the earlier work on Ho in AlAg, the transition was accompanied by a sharp solubility dip, and similar effects could influence the apparent width of the observed transition in the present case. However, the results for Gd in pure Ga establish that the

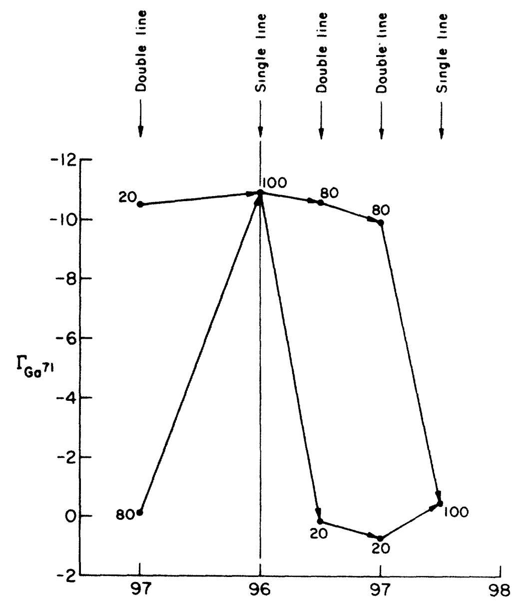

FIG. 8. Ga^{71} resonance shifts for a series of alloys in which the composition was changed in order to pass through the coupling transition (arrows in the figure indicate the sequence).

coupling transition can be no more than ~3 at.% wide.

III. DISCUSSION

In discussing the observed coupling transition, we first remind the reader that the magnetic properties of rare-earth elements show that specific, fully occupied $4f$ orbitals are LS coupled into many-electron structures very similar to those of free ions. For a one-electron description of the host band states, the complete occupancy of impurity orbitals thus established leaves only two alternatives: the core orbitals may be bound at energies below the host band bottom, or they may occur as full virtual levels degenerate with, and exchanging electrons with, the host band states. No conceptual difficulty arises when the $4f$ levels form bound orbitals and interact only weakly with the band, for these one-electron orbitals may be coupled together into a many-body configuration and then allowed to interact perturbatively with the conduction band (including the rare-earth valence states). This limit is well described by RKKY theory, and the theory provides a good description of the pure rare-earth metals, which are believed to have rather narrow conduction bands.

It seems most likely that the weak coupling observed in the Ga-rich solutions described in Sec. II E corresponds to the conventional RKKY limit, as suggested in earlier studies.[4,5] This is consistent with the emergence of weak coupling in hosts having small conduction bandwidths, for which the rather deeply bound $4f$ levels would naturally tend to fall below the host band edge. NMR studies in solid samples at low temperatures could possibly confirm the existence of RKKY-like spin-density oscillations surrounding the impurities.

Greater difficulties appear in the case of the strong-coupling observed in Al-rich solvents. The coupling to the conduction band is very large, and the spin-density disturbance is comparable in size to that produced by $3d$ impurities in Cu. Stupian and Flynn[3] point out that the magnitude is consistent with $4f$ virtual levels ~0.5 eV wide located near the Al Fermi level. However, it is difficult to eliminate completely the possibility that the spin-density disturbance originates in a lesser perturbation, which modifies the host band states over a wider bandwidth of states. An example would be the interband mixing mechanism proposed by Watson *et al.*[11] A detailed discussion of the alternative mechanisms is presented by Rigert and Flynn.[6] Either explanation requires a substantial perturbation of f-like band states caused by the exchange of electrons between conduction f orbitals and the $4f$ core levels. The existence of such a mixing is not, perhaps, too surprising since the Al conduction band edge lies at ~ − 17 eV, but quantitative theories are still lacking and a precise analysis cannot be made. We note here that the many-body $4f$ core structure is fundamentally incompatible with the phase-shift analysis required to describe a strong perturbation of band states in one-electron terms. There is, in fact, no way that the complex lanthanide core structure can be matched onto one-electron orbitals describing the conduction band; mean field couplings appear to be the only present recourse. A more elaborate theoretical scheme is evidently needed to describe strong-coupling when perturbation theory fails.

One direct insight into the complexity of the conduction-electron interaction with rare-earth cores in Al is currently available from experimental results. Electron spin resonance[12,13] results show unequivocally that the exchange coupling is positive at E_F, as expected on physical grounds. However, the Knight shift indicates a large negative coupling constant when interpreted in perturbative RKKY theory. This is not the consequence of "excluded volume" effects as has been suggested,[12] since these were carefully taken into account during the interpretation of the Knight-shift results. Rather, the discrepancy probably shows that the coupling at E_F, which alone is measured in the electron-spin-resonance work, is *not* the factor determining the solvent Knight-shift change. The latter data undoubtedly probe the rare-earth-induced perturbation deeper in the conduction band, as originally suggested by Stupian and Flynn.[3]

The transition from weak to strong coupling observed in this work also presents unresolved difficulties and cannot be fully analyzed in the absence of a sound theory of the strong-coupling limit. In earlier studies the transitions were found to be broadened over the region of a solubility anomaly that pointed clearly to the existence of two thermally accessible impurity configurations. The energy of the strong-coupling configuration favored in the Al-rich alloys crossed that of the weak-coupling configuration, and the coupling transition was spead over the range ~$2kT$ of thermal degeneracy. In the present work the transition appears so sharp that a similar explanation may encounter difficulty. However, since the Gd solubility near the transition is not known, it nevertheless remains possible that the sharpness is caused in part by Gd insolubility in a narrow composition range near 97-at.% Ga. If this is not the case, then an abrupt change in thermal balance between competing configurations near the transition could only be caused by a remarkably large composition dependence of the energy for one or both configurations. These possibilities must, of course, remain purely conjectural until Gd solubility data near the transition become available.

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