144.
[18]E. W. Plummer and A. E. Bell, J. Vac. Sci. Technol. 9, 583 (1972).
[19]S. Doniach and M. Šunjić, J. Phys. 3, 285 (1970).
[20]G. K. Wertheim and S. Hüfner, Phys. Rev. Lett. 35, 53 (1975); N. J. Shevchik, Phys. Rev. Lett. 33, 1336 (1974).
[21]B. Lundqvist, Phys. Kondens. Mater. 9, 236 (1969); R. Manne and T. Åberg, Chem. Phys. Lett. 7, 282 (1970).
[22]N. Egede Christensen and B. Feuerbacher, Phys. Rev. B 10, 2349 (1974).

Nonuniqueness of Freezing Temperature of Spins in Binary Alloys

A. P. Murani
Institut Laue-Langevin, 38042 Grenoble Cedex, France
(Received 20 April 1976)

Small-angle neutron scattering measurements on *Au*Fe alloys containing 10 and 13 at.% Fe are reported. These show a series of q-dependent freezing temperatures [sharp discontinuities in the forward scattering intensity $I(q)$ as a function of T] in contrast to a unique freezing temperature (sharp cusp) observed in the low-field magnetic susceptibility of the alloys.

Spin-glasses or binary alloys such as *Cu*Mn, *Au*Fe consisting of a small concentration of magnetic atoms (e.g., Mn, Fe) distributed substitutionally and randomly in a nonmagnetic metallic matrix (e.g., Cu, Au) have been the subject of renewed theoretical interest recently since the discovery of sharp cusps in their low-field magnetic susceptibility[1] which provide additional support to the "sharp transitions" observed in their Mössbauer hyperfine spectra.[2]

There is a growing tendency to interpret the sharp cusp as indicating a magnetic phase transition and indeed several apparently successful theoretical attempts have been made in this direction.[3] There remain, nevertheless, unexplained complexities, such as the specific heat which shows a broad maximum instead of a sharp, λ-type anomaly predicted theoretically.[4] The idea of a sharp magnetic phase transition in a system consisting of spins distributed randomly and interacting via the long-range oscillatory Ruderman-Kittel-Kasuya-Yosida exchange interaction is physically not very obvious, and other interpretations of the observed physical properties could also be considered.

Magnetic susceptibility data on many spin-glasses, such as *Au*Fe for example, show that the spins are correlated to a certain degree into superparamagnetic clusters well above the freezing temperature.[5] This is an important characteristic of spin-glasses in general which may be explained in simple terms. Within a random substitutional solid-solution system there are wide, statistical fluctuations in concentration of solute atoms over a suitably chosen microscopic scale. Spins within the more concentrated regions become correlated, in general without particular directional order, when their interaction energy $H_{\rm int}$ becomes comparable to or greater than the thermal energy kT. Such regions of correlated spins evolve progressively in size with decreasing temperature as more distant spins also become correlated resulting in an increase of the anisotropy energy E_a of the magnetic clusters which will be related in some way to the total number of spins within them. At any finite temperature the spin system may be considered as subdivided into interacting regions of correlated spins, or magnetic clusters, of various sizes. In the framework of the Néel theory of superparamagnetism,[6] the relaxation time of a particle consisting of a number of correlated spins varies exponentially with its anisotropy energy E_a and the inverse temperature $1/T$ as given by the formula

$$\tau = \tau_0 \exp(E_a/kT), \tag{1}$$

where τ_0 is some characteristic relaxation rate of the spins and k the Boltzmann constant.

As in the case of superparamagnetic particles, when the relaxation time τ becomes long compared with the "measurement time" the magnetic clusters will appear frozen, such that the magnetic susceptibility, for example, will no longer follow the Curie-Weiss behavior. This idea has been applied previously to a discussion of magnetic properties of *Au*Fe alloys[7] and more recently in a semiqualitative theory of spin-glasses by Smith.[8]

The above arguments lead us to expect a whole

series of freezing temperatures in spin-glasses corresponding to a distribution of magnetic cluster sizes. At first sight this appears to be in contradiction with the single, sharp "transition" observed in the susceptibility measurements. The latter, however, is a macroscopic quantity whose response will be dominated by the largest clusters. The sharpness of the transition, we argue, reflects merely the exponential variation of the relaxation time with $1/T$ and the fact that the anisotropy energy E_a is itself a strong function of the temperature. According to the Néel formula, the smaller clusters in the system should freeze at lower temperatures. It should be possible to observe their freezing by microscopic measurements such as with neutrons. Evidence of a distribution of freezing temperatures is present even in Mössbauer-effect measurements where the hyperfine spectra are broadened over a small but finite temperature range close to the dominant freezing temperature.[2]

Results of small-angle neutron scattering measurements of two *Au*Fe alloys containing 10 and 13 at.% Fe are reported below which show a series of discontinuities in the forward scattering intensity. Despite the large solute concentrations and the tendency to class these separately from the more dilute alloys, we believe the alloys to be representative of spin-glasses, in at least the fact that they too show single sharp cusps in their low-field magnetic susceptibility.[1] The choice of the concentrations was mainly influenced by practical considerations of performing the measurements in reasonable periods of time, possible here since the alloys develop large strongly temperature-dependent susceptibilities owing to the predominantly ferromagnetic correlation among the spins, in the evolving magnetic clusters, at these concentrations.[9]

The samples were prepared by arc melting appropriate amounts of Au (99.999%) and Fe (99.995%) metals, followed by a homogenizing anneal in vacuum at 900°C for 1 d and quenching into water. The buttons were then forged into plates 0.5 mm thick and finally reannealed at 900°C for a further day and water quenched just prior to transferring into the cryostat for the measurements. These were made in the q range 5×10^{-3} tp 30×10^{-3} Å^{-1} using a highly collimated neutron beam (0.3°) of wavelength 7.3 Å ($\Delta\lambda/\lambda$ ~8% full width at half-maximum). After scattering from the sample, the neutrons were detected on a multidetector grid of 64×64 (1 cm^2) elements placed at a distance of 10 m in an evacuated flight tube.[10] The data were evaluated by taking radial integrals of the intensity about the primary-beam center. Use of quartz windows in the cryostat helped to keep the small-angle scattering from its walls to a minimum; corrections for this were nevertheless applied to the data.

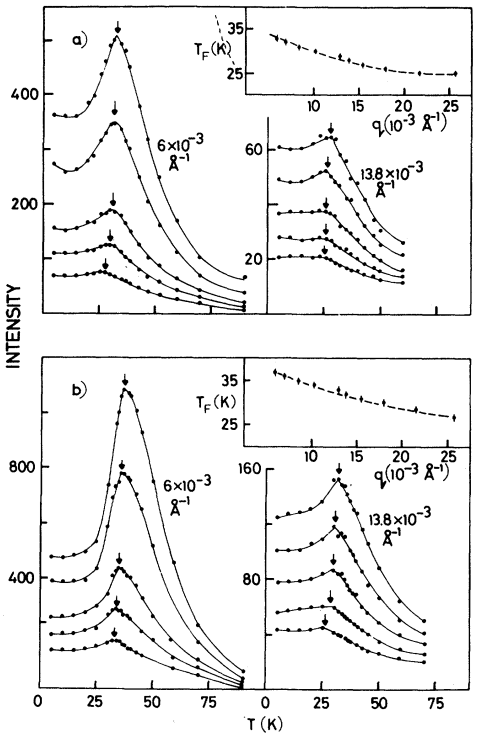

FIG. 1. Forward scattering intensity as a function of temperature for a series of q values for *Au*Fe alloys containing (a) 10 at.% Fe and (b) 13 at.% Fe. The arrows mark the temperatures T_F of the discontinuities in the scattering. These are shown plotted versus q in the insets.

Results are shown in Fig. 1 where the intensity of the scattered neutrons is plotted as a function of temperature for a range of q values. The observed scattering is almost entirely magnetic, since the nuclear scattering contribution is very small, as shown by the fact that the scattering at room temperature was very much smaller in comparison. Curves drawn through the data points resemble critical scattering peaks observed in normal ferromagnetic systems, but are different from the latter in one important respect. Instead of a single, unique temperature for the peaks (for a range of small q values), one observes here a series of q-dependent temperatures. These are shown plotted as a function of q in the insets in Fig. 1.

For a normal ferromagnetic system close to

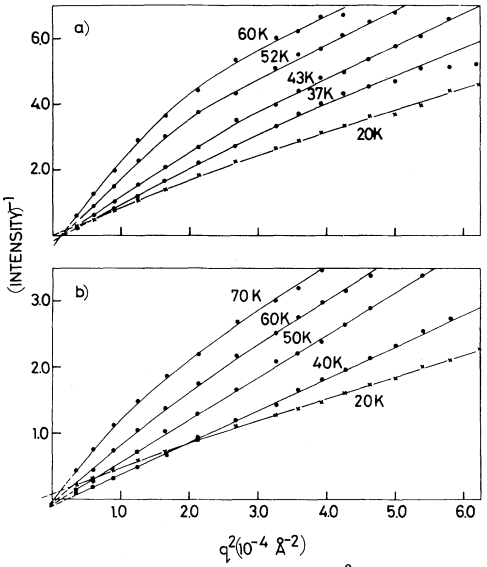

FIG. 2. Inverse intensity versus q^2 for the (a) 10-at.% Fe and (b) 13-at.% Fe alloys. Note the positive intercepts on the q^2 axis.

the critical temperature where the fluctuations are slow, the total scattered intensity (i.e., integrated over energy) for small q is given by[11]

$$I = \frac{I_0}{r_1^2(\kappa_1^2 + q^2)}, \tag{2}$$

where I_0 is a constant, r_1 the strength of the interaction, and κ_1 the inverse correlation range.

A direct verification of the different character of the observed scattering from normal ferromagnetic critical scattering is obtained by plotting the inverse intensity $I^{-1}(q)$ against q^2, Fig. 2. At higher temperatures, the data points lie on curves which become straighter with decreasing temperature. However, they give small positive intercepts on the q^2 axis except at the lower temperatures (around 30 K and below) when the intercepts are closer to zero (or negative). Clearly, the simple Ornstein-Zernike correlation function is not adequate to describe the scattering in these alloys. Allowance for the finite q resolution of the measurements has marginal effect on the curves, nor is an improved fit obtained by inclusion of the Fisher exponent[12] η; in all events the finite positive intercepts still remain.

These intercepts are interesting since they suggest that the scattering cross section goes through a maximum at a small but finite q value, which increases with decreasing temperature, and at some stage (i.e., below the temperature of the first discontinuity), begins to approach zero again. In terms of our magnetic-cluster model, it would appear that the form factors of the clusters in their "paramagnetic" state are strongly peaked in the forward direction at some characteristic q values, but that these "peaks" shift to zero when the clusters freeze out. The drop in intensity below the freezing temperature may be interpreted in terms of this shift, together with the possibility that once frozen, the different parts of the same large cluster are equivalent and act independently, with a consequent redistribution of its form factor. In this connection, it is interesting to note the gradual change of character of the intensity versus temperature curves with increasing q value below the sharp anomalies (Fig. 1). In particular, the flat, temperature-independent cross section for q values above $\sim 16\times10^{-3}$ Å^{-1} for the 10-at.% Fe alloy and $\sim 22\times10^{-3}$ Å^{-1} for the 13-at.% Fe alloy further supports the idea of redistribution of the form factors of the larger clusters on freezing.

Although calculation of the exact form factor of a cluster would require detailed knowledge of the spatial distribution of spins within a cluster, a simple model calculation assuming a constant density μ_0 of net spin moment (i.e., up minus down) gives

$$\begin{aligned} F_\alpha(q) &= A\int_0^{R_\alpha}(\mu_0/qr)\sin qr\, r^2\, dr \\ &= (A\mu_0/q^3)(\sin qR_\alpha - qR_\alpha\cos qR_\alpha), \end{aligned} \tag{3}$$

where A is a constant and R_α the radius of the cluster α. This gives $F_\alpha(0) \propto R_\alpha{}^3$ and an effective cutoff range of a cluster of radius R_α as $q \sim \pi/R_\alpha$.

The present results suggest, of course, that the form factor of a cluster is strongly peaked in the forward direction at a finite q value. This, together with a sharp cutoff range $\sim\pi/R$ of a cluster, suggests that the scattering at any given q will be dominated by clusters of some characteristic size, say $R \sim 1/q$. Results in Fig. 1 may then be seen to be in qualitative agreement with the Néel formula, since the temperatures of the discontinuities in the scattering have an inverse relationship with q, i.e., the larger clusters (small q) having larger anisotropy energy freeze at the higher temperatures. As remarked earlier, the sharpness of the freezing anomaly reflects the exponential variation of the relaxation time with the reciprocal temperature and the anisotropy energy E_a which is itself a strong function of the temperature.

In conclusion, the present results demonstrate the existence of a series of freezing temperatures

in binary alloys, which supplements (rather than contradicts) the observation of a single sharp cusp in the susceptibility, a macroscopic quantity. It is apparent that the spin system in the alloys becomes localized into finite magnetic clusters whose relaxation times influence the observed physical properties at finite temperatures well before spins can become correlated over an infinite-range scale at a lower or perhaps at zero temperature.

The author thanks Professor B. R. Coles and Dr. T. J. Hicks for helpful discussions and Dr. H. E. N. Stone for preparation of the samples.

[1]V. Cannella and J. A. Mydosh, Phys. Rev. B 6, 4220 (1972).

[2]C. E. Violet and R. J. Borg, Phys. Rev. 149, 540 (1966); B. Window, G. Longworth, and C. E. Johnson, J. Phys. C 3, 2156 (1970).

[3]K. Adkins and N. Rivier, J. Phys. (Paris), Colloq. 35, C4-237 (1974); S. F. Edwards and P. W. Anderson, J. Phys. F 5, 965 (1975); K. H. Fischer, Phys. Rev. Lett. 34, 1438 (1975); D. Sherrington and B. W. Southern, J.Phys. 5, L49 (1975).

[4]L. E. Wenger and P. H. Keesom, Phys. Rev. B 11, 3497 (1975).

[5]V. Cannella, in *Amorphous Magnetism*, edited by H. O. Hooper and A. M. de Graff (Plenum, New York, 1973), pp. 195–206.

[6]L. Néel, C. R. Acad. Sci. 228, 664 (1949).

[7]A. P. Murani, J. Phys. F 4, 757 (1974).

[8]D. A. Smith, J. Phys. F 5, 2148 (1975).

[9]A. P. Murani, S. Roth, P. Radhakrishna, B. D. Rainford, B. R. Coles, K. Ibel, G. Göltz, and F. Mezei, J. Phys. F 6, 425 (1976).

[10]K. Ibel, to be published.

[11]W. Marshall and R. D. Lowde, Rep. Prog. Phys. 31, 705 (1968).

[12]M. E. Fisher, J. Math. Phys. (N.Y.) 5, 944 (1964).

Acceptor Resonances in $Hg_{1-x}Cd_xTe$†

L. Liu*

Laboratoire de Physique des Solides, Centre National de la Recherche Scientifique, 92190 Meudon, France, and Department of Physics,‡ Northwestern University, Evanston, Illinois 60201

and

C. Vérié

Laboratoire de Physique des Solides, Centre National de la Recherche Scientifique, 92190 Meudon, France

(Received 17 May 1976)

Invoking some gross features of the band structure, we show that the resonance energy in the mixed crystal $Hg_{1-x}Cd_xTe$ as a zero-gap semiconductor should increase continuously as the molar fraction of CdTe increases. The increase becomes very strong near the point where an energy gap begins to open up in the alloy. This prediction is in qualitative agreement with experiments. We also give comments on two different models for explaining some observed conductivity anomalies.

The localized electronic states in zero-gap semiconductors become resonances because of their interaction with the continuous band states. This problem has attracted considerable attention[1-11] especially after evidence for their existence showed up in transport measurements. Some nonmonotonic dependence on temperature in the electronic conductivity was experimentally found[8-11] in HgTe and $Hg_{1-x}Cd_xTe$ mixed crystals. For example, in certain samples[8] of HgTe, anomalous conductivity dips occur around 1 K (A_0), 9 K (A_1), and 32 K (A_2). The A_1 and A_2 anomalies have been interpreted by Finck *et al.*[8] as due to scattering of conduction electrons by acceptor resonance states associated with mercury vacancies. Since the acceptor state interacts with a conduction band which has a low density of states, it can have sufficiently narrow width to become a true resonance. In spite of the fact that this model has been successful in explaining experimental findings so far,[7,8] an alternative has been proposed which interprets the A_2 anomaly as due to resonant scattering by optical phonons.[12] Based only on some gross features of the electronic energy bands, we show in this Letter that the resonance state produced by a short-range potential, as appropriate for vacancies, should undergo a continuous upward shift in energy in mixed crystals of $Hg_{1-x}Cd_xTe$ as the molar fraction of CdTe is increased from $x=0$ up to the point where the