ear interactions, so that to that extent we do confirm Levy and Chen's original hypothesis. However, the ratio of quadrupole-to-dipole terms must be such that there is a single *first-order* transition.[8] Indeed, using the experimental information reported here it should be possible to construct a complete theory for DySb in the molecular field approximation thus yielding explicit values for the quadrupole-quadrupole and dipole-dipole coupling coefficients.

Finally, we should comment briefly on the microscopic origins of the biquadratic terms in DySb. Levy and Chen regard the quadrupole-quadrupole terms as being primarily intrinsic, originating mainly in indirect coupling via the conduction electrons, with the distortions in the ordered phase then following after the fact as a result of the quadrupole-strain coupling. Alternatively, however, the biquadratic interaction could result from virtual-phonon exchange via the quadrupole-lattice coupling so that the transition would then be a cooperative Jahn-Teller and magnetic transition similar to that in UO_2.[9] First-principles or empirical estimates of the various mechanisms are not sufficiently reliable to decide between these two alternatives.[10] Additional experiments on DySb, such as velocity-of-sound measurements, inelastic neutron scattering studies of the elementary excitations, and/or spin-resonance measurements of Dy^{3+} in YSb as a function of strain, should provide the requisite information. We hope that the work reported here will serve to stimulate such additional theoretical and experimental efforts on this most interesting material.

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[1]H. H. Chen and P. M. Levy, Phys. Rev. Lett. 27, 1383 (1971); P. M. Levy and H. H. Chen, Phys. Rev. Lett. 27, 1385 (1971).

[2]F. Lévy, Phys. Kondens. Mater. 10, 86 (1969).

[3]For a review see M. T. Hutchings, Solid State Phys. 16, 227 (1964).

[4]K. C. Turberfield, L. Passell, R. J. Birgeneau, and E. Bucher, Phys. Rev. Lett. 25, 752 (1970); R. J. Birgeneau, E. Bucher, L. Passell, and K. C. Turberfield, Phys. Rev. B 4, 718 (1971).

[5]G. Busch and O. Vogt, J. Appl. Phys. 39, 1334 (1968); G. Busch, O. Marinček, A. Menth, and O. Vogt, Phys. Lett. 14, 262 (1965).

[6]V. D. Gorobchenko, I. I. Lukoshevich, V. G. Stankevich, N. I. Filippov, V. I. Chikalin, and E. I. Yarembash, Fiz. Tverd. Tela 13, 1085 (1971) [Sov. Phys. Solid State 13, 901 (1971)].

[7]Full details are given in G. P. Felcher, T. O. Brun, R. J. Gambino, and M. Kuznietz, to be published.

[8]For a complete discussion of the various possible transitions, see J. Sivardiere and M. Blume, Phys. Rev. B 5, 1126 (1972).

[9]S. J. Allen, Jr., Phys. Rev. 166, 530 (1968).

[10]For a discussion of the difficulties inherent in such estimates, see R. J. Birgeneau, M. T. Hutchings, J. M. Baker, and J. D. Riley, J. Appl. Phys. 40, 1070 (1969).

Evidence for Antiferromagnetism in Invar at High Pressures*

David R. Rhiger and R. Ingalls
Department of Physics, University of Washington, Seattle, Washington 98105
(Received 14 February 1972)

A new phase, most probably antiferromagnetic, is revealed in Invar at high pressures by Mössbauer experiments. In $Fe_{0.70}Ni_{0.30}$ the Néel temperature has a slope of $+1.9\pm0.3$°K/kbar with a zero-pressure intercept of -41 ± 21°K.

There appears to be renewed theoretical interest in the magnetic behavior of concentrated transition-metal alloys as well as the pure metals.[1] Of particular interest is their "localized" versus "itinerant" magnetic character.[2] Invar is interesting in this connection, because, although it appears to be a good example of weak itinerant electron ferromagnetism,[3] we find a localized picture quite appealing in terms of the high-pressure behavior.

Invar is also of interest for its numerous anomalies, which have been the subjects of many recent experiments. In the $Fe_{1-x}Ni_x$ binary alloy system, Invar has $0.29 \leq x \leq 0.45$ with a face-centered cubic structure. Every physical property involving magnetism or volume behaves anomalously in the Invar region compared with the rest of the fcc (γ) range, which extends from In-

var to pure Ni. Anomalies include low Curie temperature,[4,5] low zero-temperature magnetization,[4] large rate of decrease of Curie temperature[6,7] and zero-temperature magnetization[8] with pressure, very small thermal expansion,[9] and high compressibility.[10] To explain these and other anomalies, several dissimilar models, some itinerant and some localized, have been proposed,[3,8,9,11] with varying degrees of success.

For our purposes we find a phenomenological description based on the localized model of Kondorskii and Sedov[8,12] to be the most useful, since the itinerant description of Invar has not yet been extended to include the possibility of antiferromagnetism. Assuming localized magnetic moments with nearest-neighbor interactions, Kondorskii and Sedov propose that (a) the Fe-Fe exchange parameter J_{FeFe} is negative (antiferromagnetic) in the fcc structure, and that (b) J_{FeFe} increases rapidly in magnitude as the lattice is compressed. Also, the Curie temperature T_c is proportional to $(1-x)^2 J_{FeFe} + 2x(1-x)J_{FeNi} + x^2 J_{NiNi}$, where x is the atomic fraction of Ni. The contribution of J_{FeFe} is opposite to the other interactions and serves to decrease T_c when x is in the Invar region.

There is good evidence for (a) from neutron scattering[13] and Mössbauer experiments[14] on γ-Fe precipitates in Cu, from susceptibility measurements,[15] Mössbauer experiments,[14,16] and neutron scattering[17] in austenitic (fcc) stainless steels, and from high-temperature susceptibility measurements of pure bulk γ-Fe.[18]

The primary justification for (b) is that in the present context it can explain the decrease of T_c with pressure. In addition, it can provide a strong decrease in the energy of ferromagnetic ordering with a decrease in volume, which, according to Bean and Rodbell,[19] would explain the small thermal expansion. Also, in fcc $Fe_{0.51}Rh_{0.49}$ (b) is consistent with the increasing stability of the antiferromagnetic phase at the expense of the ferromagnetic phase with increasing pressure.[20]

In this Letter we consider the magnetic state of Invar at very high pressures. We believe that as the pressure increases, J_{FeFe} eventually becomes strong enough to dominate, causing the magnetic order to switch from ferromagnetic to antiferromagnetic. This should happen at some pressure for which T_c has been reduced substantially below room temperature. Above this pressure there will be a Néel temperature that rises with increasing pressure. Although several authors have discussed both points (a) and (b), or discussed Invar in terms of a state that is mostly ferromagnetic with small antiferromagnetic inclusions, none have made the extrapolation to an antiferromagnetic state at high pressures. To observe this new magnetic phase we have done Fe^{57} Mössbauer experiments on Invar using high-pressure techniques described elsewhere[21] with pressure calibrations based on the bismuth III $\rightarrow$ V transition at 75 kbar. At zero pressure and room temperature our Invar sources exhibited the same spectra as reported by other authors.[22]

For $Fe_{0.70}Ni_{0.30}$ we have taken $T_c = 368$°K at $P = 0$ (zero pressure) by interpolation of the data of Bolling, Arrott, and Richman,[5] and we have taken $dT_c/dP = -4.6$°K/kbar by interpolation of the data of Leger[7] to plot T_c versus P in Fig. 1. Magnetic phase boundaries for this alloy should be linear to a good approximation because T_c is linear up to 55 kbar for $Fe_{0.71}Ni_{0.29}$.[23]

$Fe_{0.70}Ni_{0.30}$ is known to undergo an irreversible martensitic transformation to the α (bcc) phase at 220°K and zero pressure.[24] Fortunately the martensite-start temperature M_s shifts by -8.5 °K/kbar with increasing pressure[25] as shown in Fig. 1. The martensite corner of the P-T phase diagram was avoided in our experiments.

For a sample of $Fe_{0.70}Ni_{0.30}$ Mössbauer spectra were obtained for several pressures at both 295 and 90°K. In addition, thermal scans were made as the sample was slowly cooled from 295 to 90°K at each pressure. In this technique[26] the absorber remains at zero velocity and total counting rate is measured as a function of temperature. Any magnetic transition should appear as a change in counting rate. The transitions

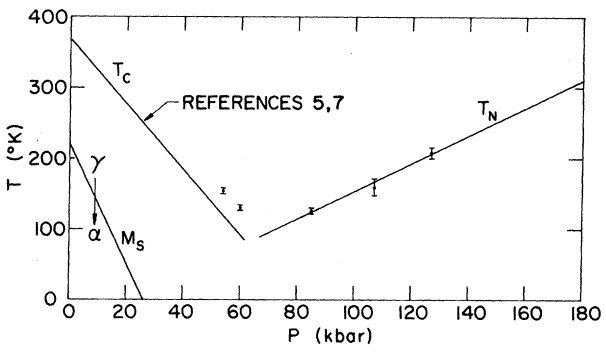

FIG. 1. Pressure-temperature phase diagram for $Fe_{0.70}Ni_{0.30}$. T_c is the Curie temperature. T_N is the proposed Néel temperature. Points with error bars are magnetic transitions determined by Mössbauer thermal scans. M_s is the martensite-start temperature.

thus determined are indicated by the points with error bars in Fig. 1.

For each of the five thermal scans (all having $P > 50$ kbar) the corresponding Mössbauer spectrum at 295°K was a single narrow line indicating paramagnetism. The corresponding spectrum at 90°K was a somewhat broader line, which we attribute to an unresolved magnetic splitting.

The transitions at 54 and 60 kbar are clearly the transition from paramagnetism to ferromagnetism. They lie above the expected phase boundary by 35 and 39°K, respectively. The difference is due in part to the presence of about 0.8% Co^{57} since 5% Co is known to raise T_c by 100°K.[27] Other sources of error lie in pressure calibration, uncertainty in dT_c/dP, and uncertainty in interpretation of the thermal scan data. The hyperfine fields observed at 54 and 60 kbar at 90°K are 7.0 ± 0.4 and 6.5 ± 0.4 kOe, respectively.

We interpret the transitions at 85, 107, and 127 kbar to be the expected transition from paramagnetism to antiferromagnetism. The thermal scan data for these are given in Fig. 2. The overall slope of the scans is due to the increasing recoilless fraction in the source and to thermal contraction of the small γ-ray window of the pressure cell with decreasing T. Although the Mössbauer spectrum shifts by almost 0.12 mm/sec between 295 and 90°K, this produces a negligible effect on the thermal scan because the zero-velocity point is near the minimum of the

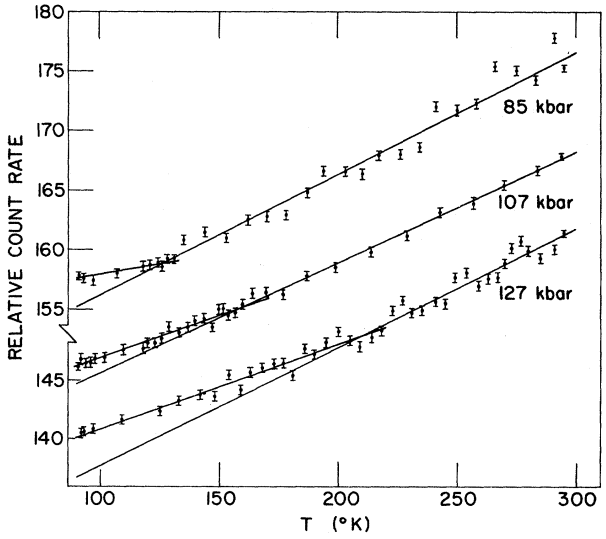

FIG. 2. Thermal scans at the indicated pressures. Straight lines are fitted as explained in the text. The line fitting the upper temperature range is extended to 90°K to illustrate the change in slope of the data.

reasonance line and because the line is rather broad (0.65 mm/sec) even when the Invar source is paramagnetic. [The main reason for this broad line is the thickness of both the source and the $Na_4Fe(CN)_6 \cdot 10H_2O$ (Fe^{57}-enriched) absorber.] For each thermal scan the counting rate can be approximated by a straight line over most of the temperature range, except at the low-temperature end where the counting rate shows a distinct rise above this straight line. This rise is of a magnitude and direction consistent with the observed 14% broadening in the corresponding Mössbauer spectrum at 90°K. Each thermal scan was analyzed in terms of a simultaneous least-squares fit of a pair of intersecting straight lines, with the temperature of intersection being one of the parameters to be fitted. The lines thus determined are plotted in Fig. 2. The temperature of intersection is chosen to be the transition temperature. It is plotted in Fig. 1 for each thermal scan at 85, 107, and 127 kbar, respectively, with an error bar determined by the statistics of the straight-line fit.

These transitions define the proposed paramagnetic-antiferromagnetic phase boundary T_N in Fig. 1. From a weighted least-squares fit of a straight line to these points, we get $dT_N/dP = +1.9 \pm 0.3$°K/kbar with an intercept at $P = 0$ of $T_N = -41 \pm 21$°K. These results have been reported earlier in brief form.[28] The line broadening seen at 90°K and $P \geq 85$ kbar is 0.092 ± 0.014 mm/sec.

With an earlier sample[29] of the same alloy containing 0.2% Co^{57}, we attempted the same experiment, but the source was too weak for the thermal scans to reveal any Néel transition. However, considering linewidths at 296 and 94°K we inferred a Néel temperature having the same slope and intercept, within experimental error, as that shown in Fig. 1.

In a preliminary run at 296°K a sample of $Fe_{0.66}Ni_{0.34}$ remained paramagnetic from 60 to 224 kbar. A thermal scan at 224 kbar revealed a transition at 225°K.[29] This indicates that as the nickel content of Invar increases, there is an increase in the pressure at which antiferromagnetism begins, and dT_N/dP decreases by roughly the same proportion as $|dT_c/dP|$.

Where T_c and T_N intersect on the P-T phase diagram, there may be a triple point below which there would be a first-order phase boundary separating the ferromagnetic and antiferromagnetic phases. This region has not yet been investigated.

We can rule out two nonmagnetic origins for the line broadening below the proposed Néel temperature. The first is the effect of the increasing self-absorption in the source due to its increasing recoilless fraction f as T decreases. In $Fe_{0.70}Ni_{0.30}$ at 110 kbar the line position shifts by 0.1175 ± 0.0012 mm/sec from 295 to 90°K. Assuming the isomer shift is temperature independent we obtain from this a Debye temperature of $\Theta = 385 \pm 10$°K. This is reasonable considering that a composition extrapolation gives $\Theta = 322$°K at $P = 0$,[30] and that Invar is quite compressible near $P = 0$.[10] From Θ we calculate f and find a line broadening of only 0.026 mm/sec.[31] Also, this effect would not produce the apparent sharp transitions seen in Fig. 2.

A second origin of broadening is a quadrupole splitting due to a possible transformation to the ϵ (hcp) phase. This phase has been seen at high pressures in $Fe_{1-x}Ni_x$ with $x < 0.21$[32] and the quadrupole splitting in ϵ-iron is 0.11 ± 0.02 mm/sec.[33] However, there should be a large thermal hysteresis between the $\gamma \rightarrow \epsilon$ and $\epsilon \rightarrow \gamma$ transformations because of the 415°K hysteresis between $\gamma \rightarrow \alpha$ and $\alpha \rightarrow \gamma$ at $P = 0$,[28] analogous to Fe-Ru alloys.[34] No hysteresis is seen in our experiment. Furthermore, for the $\gamma \rightarrow \epsilon$ transformation we would expect an isomer shift similar to that for $\gamma \rightarrow \epsilon$ in iron, about 0.1 mm/sec[35] (opposite to the thermal shift due to decreasing T at constant P). As we have seen, the total observed shift can be reasonably considered a thermal shift. We therefore conclude that we have discovered a new magnetic phase in Invar.

The hyperfine field is obtained by subtracting the self-absorption broadening from the total broadening. The result is 2.0 ± 0.5 kOe at 90°K and $P \geq 85$ kbar. This is smaller than the 17.5-kOe[16] and 21-kOe[14] fields observed in antiferromagnetic stainless steels, and smaller than the 10-kOe field observed in antiferromagnetic fcc $Fe_{0.65}Ir_{0.35}$.[36,37] This may be because our measurements are not made near $T = 0$, or because of the presence of the strong positive J_{FeNi} interaction which opposes the overall antiferromagnetic order. A small hyperfine field would also justify the assumption of a negligible isomer shift difference (at constant P) between the paramagnetic and antiferromagnetic phases.

We have not, of course, proved what type of magnetic ordering the new phase has, but antiferromagnetism is most likely. A quantitative extension[28,38] of the model of Kondorskii and Sedov, assuming antiferromagnetic order of the first kind (the same as seen in γ-Fe precipitates in Cu[13] and in fcc stainless steels[17]), predicts *approximately the same pressure and concentration dependence* of T_N as we find experimentally. If an itinerant description can be extended to yield similar results, it may have interesting consequences for another weak itinerant electron ferromagnet, $ZrZn_2$, in which T_c was seen to go to 0°K at 8.5 kbar with apparently no other magnetic order up to 25 kbar.[39]

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[1]H. Hasegawa and J. Kanamori, J. Phys. Soc. Jap. 31, 382 (1971); K. J. Duff and T. P. Das, Phys. Rev. B 3, 192 (1971); K. Levin, R. Bass, and K. H. Bennemann, Phys. Rev. Lett. 27, 589 (1971).

[2]P. J. Schurer, G. A. Sawatzky, and F. van der Woude, Phys. Rev. Lett. 27, 586 (1971); G. Busch, M. Campagna, and H. C. Siegman, Phys. Rev. B 4, 746 (1971); J. E. Rowe and J. C. Tracy, Phys. Rev. Lett. 27, 799 (1971).

[3]E. P. Wohlfarth, Phys. Lett. 31A, 525 (1970), and references listed therein.

[4]J. Crangle and G. C. Hallam, Proc. Roy. Soc., Ser. A 272, 119 (1963).

[5]G. F. Bolling, A. Arrott, and R. H. Richman, Phys. Status Solidi 26, 743 (1968).

[6]R. C. Wayne and L. C. Bartel, Phys. Lett. 28A, 196 (1968).

[7]J. M. Leger, thesis, University of Paris, 1970 (unpublished).

[8]E. I. Kondorskii and V. L. Sedov, J. Appl. Phys. 31, 331S (1960).

[9]Y. Tanji, J. Phys. Soc. Jap. 31, 1366 (1971).

[10]Y. Tanji, Y. Shirakawa, and H. Moriya, Sci. Rep. Res. Inst. Tohoku Univ. Ser. A 22, 84 (1970).

[11]W. F. Schlosser, J. Phys. Chem. Solids 32, 939 (1971), and references listed therein; G. M. Graham and R. W. Cochrane, Phys. Rev. 184, 543 (1969); D. A. Colling and M. P. Mathur, J. Appl. Phys. 42, 5699 (1971).

[12]E. I. Kondorskii, Zh. Eksp. Teor. Fiz. 37, 1819 (1959) [Sov. Phys. JETP 10, 1284 (1960)].

[13]G. J. Johansen, M. B. McGirr, and D. A. Wheeler, Phys. Rev. B 1, 3208 (1970).

[14]U. Gonser, C. J. Meechan, A. H. Muir, and H. Wiedersich, J. Appl. Phys. 34, 2373 (1963).

[15]R. Kohlhaas, A. A. Raible, and W. Rocker, Z. Angew. Phys. 30, 254 (1970).

[16]L. D. Flansburg and N. Hershkowitz, J. Appl. Phys. 41, 4082 (1970).

[17]Y. Ishikawa, Y. Endoh, and T. Takimoto, J. Phys. Chem. Solids 31, 1225 (1970).

[18]M. Fallot, J. Phys. Radium 5, 153 (1944).
[19]C. P. Bean and D. S. Rodbell, Phys. Rev. 126, 105 (1962).
[20]R. C. Wayne, Phys. Rev. 170, 523 (1968).
[21]D. L. Williamson, S. Bukshpan, R. Ingalls, and H. Shechter, to be published.
[22]C. E. Johnson, M. S. Ridout, and T. E. Cranshaw, Proc. Phys. Soc., London 81, 1079 (1963); Y. Nakamura, M. Shiga, and N. Shikazono, J. Phys. Soc. Jap. 19, 1177 (1964).
[23]J. M. Leger and C. Susse-Loriers, Phys. Lett. 37A, 145 (1971).
[24]L. Kaufman and M. Cohen, Trans. AIME 206, 1393 (1956).
[25]J. R. Patel and M. Cohen, Acta Met. 1, 531 (1953).
[26]D. G. Howard, B. D. Dunlap, and J. G. Dash, Phys. Rev. Lett. 15, 628 (1965).
[27]O. A. Khomenko, Fiz. Metal. Metalloved. 26, 269 (1968) [Phys. Metals Metallogr. (USSR) 26 (2), 84 (1968)].
[28]D. R. Rhiger and R. Ingalls, Bull. Amer. Phys. Soc. 16, 849 (1971); the value of dT_N/dP should be replaced by the value in the present Letter.
[29]D. Rhiger, R. Ingalls, and D. L. Williamson, Bull. Amer. Phys. Soc. 15, 1360 (1970).
[30]D. I. Bower, E. Claridge, and I. S. T. Tsong, Phys. Status Solidi 29, 617 (1968).
[31]S. Margulies and J. R. Ehrman, Nucl. Instrum. Methods 12, 131 (1961).
[32]C. M. Fowler, F. S. Minshall, and E. G. Zukas, in *Response of Metals to High Velocity Deformation*, edited by P. G. Shewman and V. F. Zakay (Interscience, New York, 1961), p. 275.
[33]D. L. Williamson, S. Bukshpan, and R. Ingalls, to be published.
[34]L. D. Blackburn, L. Kaufman, and M. Cohen, Acta Met. 13, 533 (1965).
[35]L. E. Millet and D. L. Decker, Phys. Lett. 29A, 7 (1969).
[36]M. Shiga, Phys. Status Solidi (b) 43, K37 (1971).
[37]In magnetically inhomogenous Fe-Ni a field of 31 kOe is reported for the antiferromagnetic regions [H. Asano, J. Phys. Soc. Jap. 27, 542 (1969)].
[38]D. R. Rhiger, to be published.
[39]T. F. Smith, J. A. Mydosh, and E. P. Wohlfarth, Phys. Rev. Lett. 27, 1732 (1971).

Identification of a Class of Disordered One-Dimensional Conductors

Aaron N. Bloch and R. Bruce Weisman*
Department of Chemistry, Johns Hopkins University, Baltimore, Maryland 21218

and

C. M. Varma†
Department of Physics and The James Franck Institute, The University of Chicago, Chicago, Illinois 60637
(Received 18 January 1972)

We find that over thirty solids having high one-dimensional conductivity form a class of materials whose electronic properties are determined principally by structural disorder.

Recently, considerable experimental work[1-7] has been reported on a number of highly conducting solids in which the propagation of electrons is confined effectively to one dimension. The most prominent examples are some of the "mixed-valence" complexes[8] of platinum and iridium, and certain salts of the organic ion-radical tetracyanoquinodimethan (TCNQ).[9] Here we recognize the central significance, for the electronic properties of these materials, of a fact which has been overlooked in previous interpretations: X-ray crystallographic data, where available,[8,11,12] show them to be structurally disordered. Indeed, this is to be expected on chemical grounds[10] for the entire class. Exact theorems have been proven[13] stating that all electronic states in any disordered one-dimensional structure are localized. The existence of such a class of materials thus acquires special significance.

Electronic conductivity in disordered one-dimensional systems can occur only by phonon-assisted hopping,[14] and we find that the available data are understood on this basis. Moreover, we find that the magnetic susceptibility, the optical properties, and the ac conductivity all consistently support the same point of view. Our work resolves certain difficulties in the treatment by Epstein *et al.*[4] of the *N*-methyl-phenazinium salt NMP–TCNQ as a realization of the one-dimensional Mott-Hubbard model, and in the interpretation by Kuse and Zeller[7] and others[5-8] of $K_2Pt(CN)_4Br_{0.3}\cdot 2.3H_2O$ as a one-dimensional metal.

It will be convenient for our purposes to divide