

Research on Magnetic Materials of Interest in Transportation

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ABSTRACT

This paper reports the results of an investigation on magnetic materials of interest in the transportation field. It includes information about the present state of magnetic materials and examines the recently discovered phenomenon referred to as colossal magnetoresistance (CMR). Magnetic materials are used directly as magnets in various applications in transportation vehicles, barrier gates, smart cards, and road sensors. For CMR materials to replace the materials referred to as giant magnetoresistance (GMR), it will be necessary to identify a CMR material that undergoes transition into a metallic state with a smaller external magnetic field at room temperature. Calculations were performed and experiments were done that allow the prediction of where the magnetic transition should occur. Our studies indicate that a compound consisting of lanthanum, manganese, oxygen, and strontium (La-Mn-O-Sr) should be a prime candidate for potential applications in transportation.

INTRODUCTION

Magnetic materials form a wide range of technical applications of interest in the transportation field. They are used directly as magnets and in computer storage mechanisms in all types of transportation vehicles. With progress in the development of technology, there will be more reliance on computer control and less on the driver of a vehicle. Magnetic materials are found in many applications, such as motors, generators, read transducers, advanced computer memory, and storage technology (mainly bubble domain memories and magnetic recording systems). Much research has been put into the development of giant magnetoresistance (GMR) materials for application in magnetic recording heads, but far less effort has been put into the very large application area of automotive sensors. The material requirements for these sensors that are mainly used in transportation environments are, however, very different from those for read heads. Robustness at higher temperatures and in large magnetic fields is often a prerequisite. Furthermore, the output signal should be large and unambiguous. Despite wide usage, magnetic materials research has not made technological breakthroughs, comparable with those found in semiconductor research. The reason lies in the relevant length scales: cooperative magnetic behavior derives from electron exchange, and the exchange lengths in most magnetic materials are only a few atomic spacings (one or two nanometers). Whereas semiconductors exhibit novel behavior at carrier lengths of tens of nanometers, magnetic material structures must be controlled at the scale of a nanometer or less. In the last few years, however, researchers have made advances in atomic-scale growth and characterization methods that have produced structures that yield fascinating new magnetic phenomena. If the mechanisms for magnetism can be better explained, then materials with stronger magnetic properties may be designed and used in various transportation applications. The physics department at Morgan State University has been conducting research on various types of magnetic materials for the past twenty years. The author has recently published a paper detailing the mechanism of magnetism and many of its applications.¹ An improvement in magnets would lead to a 15% improvement in electric motors. Electric motors use two-thirds of the power in this country. This paper reviews current application of magnetic materials in transportation and examines the possibility of using future developments in colossal magnetoresistance (CMR) materials for transportation applications.

Present State of Magnetic Materials in Transportation

Magnetic materials presently find many applications in transportation. Figure 1 shows 35 locations on an automobile where magnetic materials are presently being used². Most of the present magnets used are ferrites or neodymium-iron-boron materials. They have transition temperatures above room temperature. There are also magnetic barrier-gate units used for controlling the entry and exit of vehicles to parking lots, buildings, or cities. Many historic towns have problems coping with traffic. This is especially true in many European cities where congestion and the resulting pollution are very troublesome, and causes damage to historic buildings and museums. Magnetic materials offer potential solutions to these and other transportation-related problems.

Magnetic devices are buried in the road coupled with magnetometers that are used to monitor traffic flow. Road sensors are also used to measure factors ranging from wind speed and air temperature to the temperature of water standing on the highway. This information can be used by highway maintenance departments and to warn drivers of conditions. A company called Nu-metrics has a permanent in-pavement designed sensor that uses vehicle magnetic imaging technology to monitor highway traffic, weather, parking complexes, and airports. These sensors are used to complete a road weather information system (RWIS), which allows one to obtain readings of road surface temperature and conditions. This information can then be used to produce temperature profile readings of the road surface temperature, which is combined with forecasts of atmospheric conditions to produce an accurate forecast of road temperature and conditions. Precise information can enable road maintainers to take appropriate road treatment measures before ice forms on roads. This improves safety and also reduces salt usage, because it takes much less salt to prevent ice from forming and bonding to the pavement than it does to melt away ice once it has formed. Studies have shown that careful monitoring of pavement temperature can produce enormous savings in road treatment costs during the winter. Salt loses its effectiveness as the temperature drops, so greater concentrations of it are needed to keep the solution liquid at colder temperatures. Agencies have to switch to some other chemical or sand below -15°C . Pavement temperatures are critically important throughout the winter, and it is necessary to keep track of the pavement temperature at all times to treat roads appropriately.

This is of great economic significance, because a large item in most US state highway agency budgets is snow and ice control.

Magnetic technology is also used in automatic highway systems where vehicles cruise along a test course guided by magnetic devices buried in the road. The devices send signals to magnetic sensors called magnetometers bolted under their front bumpers. The motion of the vehicle is then monitored by a computer in the car. Refinement of this system is not complete, but the system is expected to be used in about 15 years. A demonstration of this system was performed in San Diego and was the result of a seven-year research effort headed by the National Automated Highway System Consortium, which is a partnership composed of industry, government, and academia. Automatic highway systems may prove useful in dealing with the increasingly high density of highway traffic. About 200 million cars are on the road, which is twice as many as 1970. However, this is only half the number predicted 20 years from now.³

Nu-Metrics has developed two traffic measurement instruments that are used to record speed and traffic volume. Vehicle measurement is done by the use of tiny, low-powered, solid-state magnetic sensors using GMR. GMR was discovered 10 years ago and is found in metallic films consisting of magnetic layers a few nanometers (10^{-9}) that are separated by equally thin non-magnetic layers. When a magnetic field is present, large decreases in the resistance of these films are observed. When the GMR sensors are used in a traffic analyzer, they output a signal that is proportional to the strength of the earth's magnetic field. Because all vehicles are manufactured with a number of ferrous (magnetic) materials, their presence and movement over the sensors interfere with the earth's magnetic lines of force. This creates a number of perturbations. Signals are then converted to a binary format when the magnetic lines change in response to a vehicle's magnetic properties. Each vehicle has its own binary signature that is analyzed by a microprocessor in determining the speed and class of the vehicle.

Another application of magnetic materials is in the utilization of "smart cards" that contain memory chips or microprocessors. Urban transport card systems currently exist in Europe, North America, and Eastern Asia. The goal of all card systems is to replace cash and reduce costs. This includes the cost of handling coins and bank notes and costs associated with security.

It is estimated that \$271,867,939 is collected per month by public transport companies in the US.⁴ Hong Kong recently introduced the world's most extensive transport smart card network: the Octopus system.⁵ In the Octopus system, smart cards give information about riders and may be used for fares and tolls. Hert Fordshire County in Britain distributed smart cards to students in 1997. These cards contain a chip that identifies the child and records information about the journey. A smart card reader records each transaction during the day in a removable memory pack, and the information is automatically downloaded. Some cards are designed to be read at a distance; hence, they mitigate queue-related incidents at tollbooths. A driver merely drives by and flashes a smart card, which is read by an electronic reading device. One bus operator has calculated that 500 fewer buses would be needed in a city the size of London because 10% of journey time can be saved with fully contactless ticketing.⁶ Additional applications include fleet management, smart tachometers, passports, and various taxi and driver services. Cards may also be used to assist with the huge workload associated with registration and fee collections. Police can be equipped with hand-held card readers to instantly monitor a driver's status.

Future—Colossal Magnetoresistance (CMR)

A further development of GMR is a recent discovery referred to as CMR. CMR materials can fulfill the requirements necessary for transportation vehicles. CMR materials have a much larger effect (hence, called colossal) and will be more sensitive than present day applications. In 1993, Jin et al.⁵ of AT&T Bell Laboratories observed a magnetoresistance effect in materials with a composition of $\text{La}_{2/3}\text{Ca}_{1/3}\text{MnO}_x$. The effect was more than three orders of magnitude larger than the typical GMR discussed previously. The researchers observed that samples that had been heat-treated exhibited magnetoresistance values as high as 127,000% near 77 K and around 1300% near room temperature. They termed this effect "colossal magnetoresistance." Later, a group of French researchers (Craigmert et al.⁶) observed a polycrystalline manganite ($\text{Sm}_{2/3}\text{Sr}_{1/3}\text{MnO}_3$) that exhibited a resistance variation up to 50,000% at 92.5 K. At present, the details of CMR are not clearly understood. For example, it is not known definitively why these materials undergo such large changes in resistance with the applications of magnetic fields and/or heat treatment. There is extensive research currently taking place to identify all the causes of these effects. Development and use of CMR materials instead of GMR would reduce substantially the cost of building and operating vehicles.

METHODOLOGY

A part of this investigation involved the use of nuclear gamma resonance spectroscopy (better known as Mössbauer spectroscopy) to gain a better understanding of these materials. The Mössbauer effect is used to study the internal properties of materials and has a wide range of applications in biology, chemistry, physics, and materials science. All materials have a structure that consists of nuclei surrounded by a cluster of moving electrons distributed over a finite volume. The energy levels of a nucleus situated in an atom and in a solid may change states, thus changing the environment of the nucleus. Mössbauer spectroscopy enables one to investigate these energy levels by measuring the resonant absorption of Mössbauer radiation. Mössbauer spectroscopy makes use of the concept of the Mössbauer effect to monitor the behavior of nuclei of materials and their environment. This effect involves the emission of gamma radiation by a nucleus causing transition of energy from its excited state to a ground state. This enables very small energy changes resulting from the hyperfine interactions between a nucleus and its surrounding electrons to be investigated. Therefore, Mössbauer spectroscopy provides a means of using the nucleus as a probe of its environment.

In a typical experiment using Mössbauer spectroscopy, a spectrometer is used to measure the radiation absorbed by a material over a spectrum of velocities. A radioactive source is mounted on a velocity transducer that imparts the timed vibrations that causes a Doppler shift of the energy. This mechanism sends low-level gamma radiation to the absorber. These gamma rays are incident to the material being studied (called the absorber). Some of the radiation is absorbed and re-emitted in all directions, whereas the remainder of the gamma radiation penetrates the absorber and is captured by a nuclear detector. The resulting Mössbauer spectrum consists of a plot of gamma radiation counts versus measurements of relative velocity of the source with respect to the absorber, usually measured in milliseconds per second. The radiation used for the source is in the form of certain isotopes that make it possible to perform Mössbauer spectroscopy. In the laboratory at Morgan State University, one can use the iron isotope ^{57}Fe from ^{57}Co or the europium isotope ^{151}Eu from a Sm_2O_3 source. This investigation was conducted using europium.

Mössbauer measurements were performed at several temperatures between 15 K and 293 K using a ^{151}Eu source. The spectrum at room temperature is a single line demonstrating paramagnetism, with an isomer shift of 0.60 ± 0.02 mm/s. Measurements at room temperature show the europium to be trivalent and single phase with a line width of 2.933 ± 0.004 mm/s, which is comparable to that found for the commonly used Mössbauer standard europium fluoride. Measurements below 100 K show a much broader line width, which at 15 K is more than twice that found at room temperature and is associated with a magnetic phase transition as the material goes from one type of magnetic interaction into another type. Mössbauer, resistivity, and magnetic measurements all indicate a change in the paramagnetic state around 230 K. This transition may be caused by effects similar to those found for the praseodymium manganite system where the magnetic properties at low temperature were determined by ordering of the $\text{Mn}^{+3}/\text{Mn}^{+4}$ ions.⁸ A part of this research effort was to look at what combination of materials could be used to synthesize a room temperature CMR compound that would be suitable for transportation purposes. This was also accomplished by reviewing the available literature on these compounds and determining which ones would have magnetic transition temperatures at or above room temperature. This was accomplished by using the data extracted from Shannon,⁹ Thomas et al.,¹⁰ Troyanchuk et al.,¹¹ and Oliver et al.¹² Tables 1 to 3 show the numerical values for all samples. Figures 4 to 7 are constructed to illustrate the relationship between magnetic transition temperature versus ion radius. Figures were also constructed to illustrate the relationship between transition temperature and mass. Figures 8 to 11 show these results.

Isomer Shift

On the display of the Mössbauer spectrometer, the position of the absorption line relative to the central marking (zero velocity) represents the isomer shift, which is sometimes called the chemical shift. Isomer shift occurs when there is a difference in the volume of a nucleus in the ground and excited states. The amount of shift depends primarily on the change in the radius of the nuclei upon excitation, which will also represent a change in energy level. The shift takes place as a result of an electric monopole (coulomb) interaction between the nuclear charge distribution over a finite nuclear volume and the electronic charge density over its volume. The isomer shift was measured in this work; then we could determine the electronic valence of the

europium by comparing results found here with the isomer shift found for known europium compounds.

Magnetic Splitting

When nuclei are placed in a magnetic field, there is a magnetic dipole interaction between the nuclear magnetic moment and magnetic field. Because the splitting of the spectral lines is directly proportional to the magnetic field experienced by the nucleus, Mössbauer spectroscopy provides a very effective means by which the field may be measured. In this work we were able to observe if and at what temperature the magnetic transition was occurring using this technique.

RESULTS

Foncuberta et al.⁷ demonstrated that one could use Mössbauer spectroscopy as a local probe of the magnetic ordering by doping at the manganese site with ⁵⁷Fe in CMR materials. They observed a magnetic transition and also a strong field-induced polarizability. In this investigation, we successfully substituted europium for lanthanum and used Mössbauer spectroscopy to investigate the interactions occurring at the rare-earth site. Our results down to 20 K show an increase in the line width, which we interpret as the beginning of the onset of one type of magnetic interaction to another type of magnetic interaction. Table 1 shows the Mössbauer results. Figure 2 is a typical Mössbauer spectrum. Figure 3 shows the temperature dependence of magnetic susceptibility.

CONCLUSIONS

In our work, the magnetic and structural properties of the bulk manganite $\text{Eu}_{2/3}\text{Ca}_{1/3}\text{MnO}_3$ were characterized using Mössbauer spectroscopy, magnetization measurements, x-ray diffraction, and resistivity measurements. It was conclusively demonstrated that one can investigate the magnetic properties of manganites using Mössbauer spectroscopy by doping with europium at the rare earth site and using gamma rays from ^{151}Eu as a probe. $\text{La}_{2/3}\text{Ca}_{1/3}\text{MnO}_3$ is known to have a magnetic transition temperature of 260 K.¹³ Substituting europium for lanthanum caused a decrease to 100 K. Thus, one needs to reduce the amount of europium substituted in a compound if one does not want to alter the properties greatly.

Structural changes also influenced the observed properties of the praseodymium system and may also contribute to the changes in the europium system.¹⁴ Although the magnetic phase change at lower temperature is suggestive of spin glass behavior and can be classified as weak or antiferromagnetic, the europium compound may also be affected by the presence of a canted magnetic state. The complex magnetic changes occurring in this system are similar to those observed in the europium strontium perovskite, where there were variant magnetic spin structures.¹⁵ The present study shows for the first time that it is possible to substitute europium at the rare earth site in manganites, obtain a relatively narrow line width at room temperature, and obtain information about the electronic and magnetic properties as a function of temperature using Mössbauer spectroscopy. The author has recently published a paper detailing the more technical aspects of this work.¹² Magnetization, in general, increases with decreasing temperature. The transition temperature of a substance, also known as the Curie temperature, is the point at which the substance loses its spontaneous magnetization. When the temperature of a ferromagnetic compound exceeds its Curie temperature, the magnetic moments are no longer aligned, the thermal energy is large enough to cause a random orientation of the dipoles and it becomes paramagnetic.

The ferromagnetic Curie temperatures for this study were taken from Thomas et al.¹⁰ They were determined by ac susceptibility measurements at 100 Hz.

Ionic radius is an important factor in determining the structure of a solid. The lattice energy and the way in which the ions pack in a solid are both dependent on ionic radius. The ionic radius depends on the number of electrons, the orbital of the outer shell electrons, and the orbital of nuclear charge. The coordination number—which is the number of bonds formed by the central metal atom to donor atoms in a coordination complex—must be considered when calculating the ionic radius. Values of the ionic radius were taken from Shannon.⁹ The oxidation number of lanthanides was +3 with a coordination number of 12 for Sm and Nd and a coordination number of 6 for Pr and Eu. The oxidation number of the other metals was +2, with a coordination number of 12. These coordination and oxidation numbers are based on an ideal perovskite structure.

A decrease in ionic radius generally resulted in a decrease in the transition temperature. Praseodymium was an exception to this trend. When the ionic radius of the A-site cation is decreased, the Mn—O—Mn bond angle is decreased, thereby modifying the Mn—Mn hopping by electrons, resulting in a decrease of transition temperature. The transition temperature depends on the nature of the substituted divalent cation. The temperature seems to decrease exponentially as the mass of the sample increases, with the exception of SmCa.

RECOMMENDATIONS

For CMR to replace GMR materials, a CMR material will have to be found where the material undergoes a transition into a metallic state with a smaller external magnetic field and at room temperature. Calculations were done in this study that allow us to predict where the magnetic transition should occur in CMR manganites. Based on experimental and theoretical calculations, we found that europium causes a decrease in the transition temperature to below that of liquid nitrogen (77 K). Our study indicates the strontium, barium, and lead series would be acceptable candidates to use as CMR compounds for use with transportation vehicles. Because lead is toxic, it is recommended that investigations should be centered on the strontium and barium compounds. Our study demonstrated that one could lower the transition temperature of a parent material by doping with other elements. Hence, with proper doping, one should be able to construct a material with a transition temperature at room temperature.

REFERENCES

1. Oliver, F. W., "Magnetism and Magnetic Materials: Current Status and Two Future Research Areas," *J. Natl. Tech. Assoc.*, Vol. 72, 36 (Fall 1998).
2. Livingston, J., *Driving Force*, Harvard Press, p. 114 (1996).
3. Shelsby, T., "Drivers Can Sit Back, Enjoy Ride," *Baltimore Sun*, 2A (June 15, 1998).
4. ITS International, p. 78, January/February (1998).
5. Jin, S., Tiefel, T., McCormack, M., Fastnacht, R. A., Ramesh, R., and Chen, L. H., "Thousandfold Change in Resistivity in Magnetoresistive La-Ca-Mn-O Films," *Science*, Vol. 264, 413-415 (1994).
6. Craignaert, V., Maignam, A., and Raveau, B. "Up to 50,000 Percent Resistance Variation in Magnetoresistive Polycrystalline Perovskites $\text{Ln}_{2/3}\text{Sr}_{1/3}\text{MnO}_3$ (Ln=Nd; Sm)," *Solid State Comm.*, Vol. 95(6), 357 (1995).
7. Fontcuberta, J., Martinez, B., Seffar, A., Pinol, S., Roig, A., Molins, E., Obradors, X., Alonso, J., and Gonzalez-Calbet, J. M., "Magnetic Properties of Colossal Magnetoresistive Manganese Oxides," *J. Appl. Phys.*, Vol. 79(8), 5182 (1996).
8. Jirak, Z., Krupicka, S., Simsa, Z., Dlouha, M., and Vratilav, S., "Neutron Diffraction Study of $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$ Perovskites," *J. Magnet. Magn. Mtrls.*, Vol. 53, 153 (1985).
9. Shannon, R. D., "Revised Effective Ionic Radii and Systematic Studies of Interatomic Distances in Halides and Chalcogenides," *Acta Cryst. Sect. A*32, 751 (1976).
10. Thomas, R. M., et al., "Transport Properties of $(\text{Sm}_{0.7}\text{A}_{0.3})\text{MnO}_3$ (A = Ca^{2+} , Sr^{2+} , Ba^{2+} , Pb^{2+})," *J. Appl. Phys.*, Vol. 81(8), 5763-5765 (1997).

11. Troyanchuk, I. O., et al., "Magnetic and Transport Properties of EuMnO_{3+x} Substituted by Ca, Sr and Cr Ions," *Phys. Stat. Sol. (a)*, Vol. 160, 195 (1997).
12. Oliver, F. W., Seifu, D., Hoffman, E., Williams, C., Kannan, E., Kebebe, A., Kutz, M., and Tessema, "Magnetic Properties of Bulk $\text{Eu}_{2/3}\text{Ca}_{1/3}\text{MnO}_3$," *J. Appl. Phys.*, Vol. 85(8), 5387 (1999).
13. Schiffer, P., Ramirez, A. P., Bao, W., and Cheong, S. W., "Low Temperature Magnetoresistance and the Magnetic Phase Diagram of $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$," *Phys. Rev. Lett.*, Vol. 75(18), 3336 (1995).
14. Barratt, J., Lees, M. R., Balakrishnan, G., and McK Paul, D., "Insulator-Metal Transitions in $\text{Pr}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ Induced by a Magnetic Field," *Appl. Phys. Lett.*, Vol. 68, 424 (1996).
15. Sundaresan, A., Maignan, A., and Raveau, B., "Spin-Glass State and Magnetic-Field-Induced Phenomena in Distorted $\text{Eu}_{0.58}\text{Sr}_{0.42}\text{MnO}_3$ Perovskite," *Phys. Rev.*, Vol. 55(9), 5596 (1974).

APPENDIX

Papers Published Resulting from Grant

1. *Journal of Applied Physics*, Volume 85(8), 15 (April 1999).
2. *Journal of The National Technical Association*, Volume 72, 36 (Fall 1998).

University/Personnel Development

1. Performed experiments (for the first time) at Morgan State University at a temperature as low as 6 K (-430°F below freezing) using a cryogenic refrigerator. Future Mössbauer measurements can now be done on a routine basis at this temperature.
2. Allowed Morgan State University to develop a consortium in magnetic studies between four universities (Morgan State University, Clemson University, North Carolina A&T, and West Virginia University). Faculty from the four institutions plan to continue working on magnetic-related research in the future.
3. Provided full financial summer support for a graduate student and Baltimore City science middle school teacher (Camille Hinmon) to do research and be listed as a co-author on a published paper and on three national presentation abstracts. Provided summer support for a second graduate student and a Northern High School physics teacher for the summer of 1999.
4. Supported Mössbauer laboratory research, which enabled a senior physics student (Brian Hallen) to be listed as a co-author on a published paper and on three national presentation abstracts.
5. Provided full financial summer support for a Northern High School student (Claude Dodson) to work on project during the summer of 1998.
6. Provided full financial summer support for a physics professor (Dr. Frederick Oliver) to be first author on two published papers and three national presentations.

7. Provided full financial summer support for two Morgan State University undergraduate physics students to work on projects during the summers of 1998 and 1999.
8. Supported Mössbauer laboratory research that enabled four Morgan State University undergraduate students (Kevin Wyatt, Maurice Stevens, Carmen Greene, and Rashaad Jones) and two high school students (Charlotte Tirado) to work on magnetic materials-related research during the summer.
9. Supported Mössbauer laboratory research that enabled four physics professors to work on magnetic materials-related research during the summer and to be listed as co-authors on a published paper and three national presentations.

Presentations Resulting from Grant

1. F. W. Oliver, D. Seifu, E. Hoffman, C. Williams, E. Kannan, A. Kebebe, M. Kutz, and G. Tessema, "Magnetic Properties of Bulk $\text{Eu}_{2/3}\text{Ca}_{1/3}\text{MnO}_3$," 43rd Annual Conference on Magnetism and Magnetic Materials, Miami, Florida, November 9-12, 1998.
2. F. W. Oliver, D. Seifu, E. Hoffman, C. Williams, E. Kannan, A. Kebebe, M. Kutz, and G. Tessema, "Magnetic and Mössbauer Studies on the Model Colossal Magnetoresistance Material $\text{Eu}_{2/3}\text{Ca}_{1/3}\text{MnO}_3$," 70th Annual National Technical Association Conference, Arlington, VA, November 20-21, 1998.
3. F. W. Oliver, D. Seifu, E. Hoffman, C. Williams, E. Kannan, A. Kebebe, M. Kutz, and G. Tessema, "Magnetic and Mössbauer Studies on the Model Colossal Magnetoresistance Material $\text{Eu}_{2/3}\text{Ca}_{1/3}\text{MnO}_3$," American Physical Society March Meeting, Atlanta, GA, March 20-26, 1999.
4. F. W. Oliver, E. Hoffman, D. Seifu, and M. S. Seehra, "Mössbauer and Magnetic Studies on EuMn_2O_5 ," American Physical Society March Meeting, Minneapolis, Minnesota, March 20-25, 2000.

TABLE 1. Mössbauer Experimental Data

Sample	Temperature	Isomer Shift (mm/s) \pm 0.02	Line Width (mm/s) \pm 0.004
EuF ₃	293	0.00	2.931
Eu _{2/3} Ca _{1/3} MnO ₃	293	0.60	0.933
	200	0.65	3.050
	150	0.68	3.011
	95	0.69	3.504
	80	0.71	3.690

TABLE 2. Parameters for Colossal Magneto-resistive Compounds

Sample	O.N. and C.N. of Lanthanide	L.R. of Lanthanide (in Å)	O.N. and C.N. of Metal	I.R. of Metal (in Å)	R _A (in Å)	T _c (in K)
(Sm _{0.7} Ca _{0.3})MnO ₃	+3 and 12	1.24	+2 and 12	1.34	1.27	115
(Nd _{0.7} Ca _{0.3})MnO ₃	+3 and 12	1.27	+2 and 12	1.34	1.29	115
(Pr _{0.7} Ca _{0.3})MnO ₃	+3 and 6	0.99	+2 and 12	1.34	1.31	117
(La _{0.7} Ca _{0.3})MnO ₃	+3 and 12	1.36	+2 and 12	1.34	1.36	220
(Eu _{0.67} Ca _{0.33})MnO ₃	+3 and 6	0.947	+2 and 12	1.34	1.09	74
(Sm _{0.7} Sr _{0.3})MnO ₃	+3 and 12	1.24	+2 and 12	1.44	1.30	70
(Nd _{0.7} Sr _{0.3})MnO ₃	+3 and 12	1.27	+2 and 12	1.44	1.32	195
(Pr _{0.7} Sr _{0.3})MnO ₃	+3 and 6	0.99	+2 and 12	1.44	1.13	311
(La _{0.7} Sr _{0.3})MnO ₃	+3 and 12	1.36	+2 and 12	1.44	1.38	370
(Sm _{0.7} Ba _{0.3})MnO ₃	+3 and 12	1.24	+2 and 12	1.61	1.35	105
(Nd _{0.7} Ba _{0.3})MnO ₃	+3 and 12	1.27	+2 and 12	1.61	1.37	145
(Pr _{0.7} Ba _{0.3})MnO ₃	+3 and 6	0.99	+2 and 12	1.61	1.18	170
(La _{0.7} Ba _{0.3})MnO ₃	+3 and 12	1.36	+2 and 12	1.61	1.44	330
(Sm _{0.7} Pb _{0.3})MnO ₃	+3 and 12	1.24	+2 and 12	1.49	1.32	96
(Pr _{0.7} Pb _{0.3})MnO ₃	+3 and 6	0.99	+2 and 12	1.49	1.35	170
(La _{0.7} Pb _{0.3})MnO ₃	+3 and 12	1.36	+2 and 12	1.49	1.40	300

O.N. = oxidation number

C.N. = coordination number

I.R. = ionic radius in Ångstroms

R_A = ionic radius of the A-site

T_c = transition temperature

Oxidation numbers and coordination numbers are based on ideal perovskite structure. Ionic radii are taken from the Shannon¹ paper.

R_A is weighted average. The lanthanide ionic radius is multiplied by 0.7, and the metal ionic radius is multiplied by 0.3.

Transition temperatures were taken from the Thomas² paper. They were determined by ac susceptibility measures at 100 Hz.

The transition temperature for (Eu_{0.67}Ca_{0.33})MnO₃ was taken from the Troyanchuk³ paper.

¹ Shannon, R. D., *Acta Cryst., Sect. A*, 32, 751 (1976).

² Thomas, R. M., et al., *J. Appl. Phys.*, 81(8), 5763 (1997).

³ Troyanchuk, I. O., et al., *Phys. Stat. Sol. (a)*, 160, 195 (1997).

TABLE 3. Molecular Weight and Transition Temperatures for Colossal Magnetoresistive Compounds

Sample	Mass (g)	Transition Temp. (K)
(Sm _{0.7} Ca _{0.3})MnO ₃	221.27	115
(Nd _{0.7} Ca _{0.3})MnO ₃	214.27	115
(Pr _{0.7} Ca _{0.3})MnO ₃	213.57	117
(La _{0.7} Ca _{0.3})MnO ₃	212.17	220
(Eu _{0.7} Ca _{0.3})MnO ₃	218.58	74
(Sm _{0.7} Sr _{0.3})MnO ₃	235.66	70
(Nd _{0.7} Sr _{0.3})MnO ₃	228.65	195
(Pr _{0.7} Sr _{0.3})MnO ₃	227.95	311
(La _{0.7} Sr _{0.3})MnO ₃	226.55	370
(Sm _{0.7} Ba _{0.3})MnO ₃	250.66	105
(Nd _{0.7} Ba _{0.3})MnO ₃	243.65	145
(Pr _{0.7} Ba _{0.3})MnO ₃	242.95	170
(La _{0.7} Ba _{0.3})MnO ₃	241.55	330
(Sm _{0.7} Pb _{0.3})MnO ₃	271.68	96
(Pr _{0.7} Pb _{0.3})MnO ₃	263.97	170
(La _{0.7} Pb _{0.3})MnO ₃	262.57	300

Figure 1. Possible applications of magnets in an automobile²

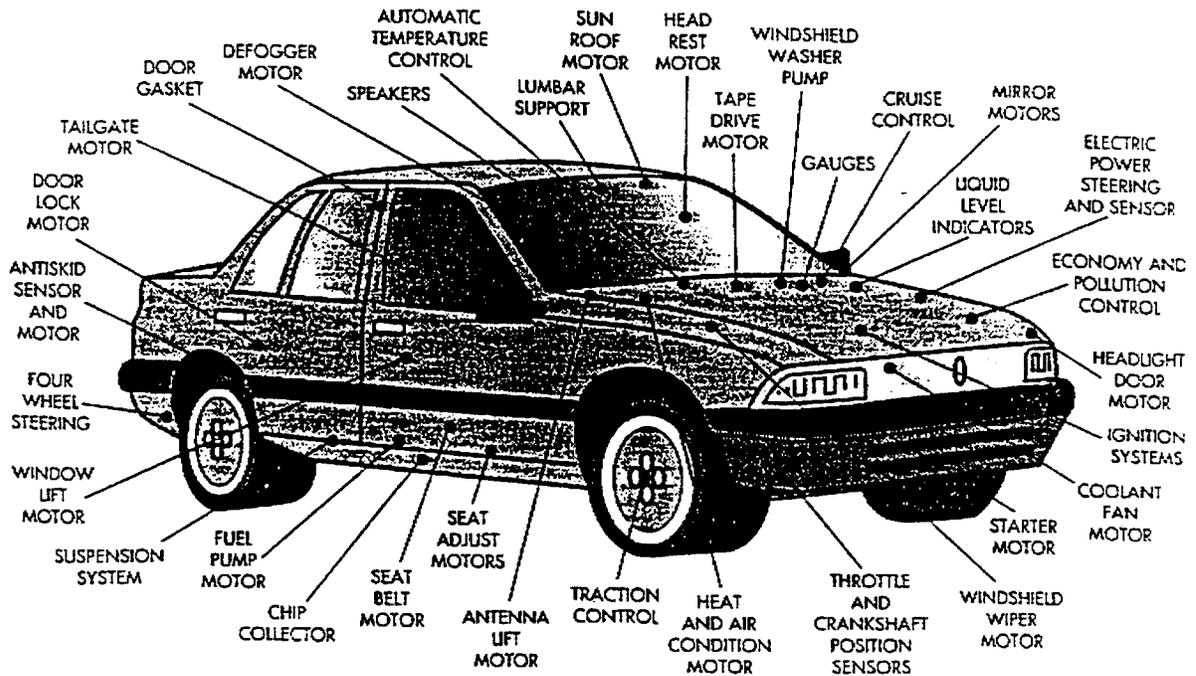


Figure 2. Mössbauer spectra at (a) 293K, (b) 80K, and (c) 20 K.

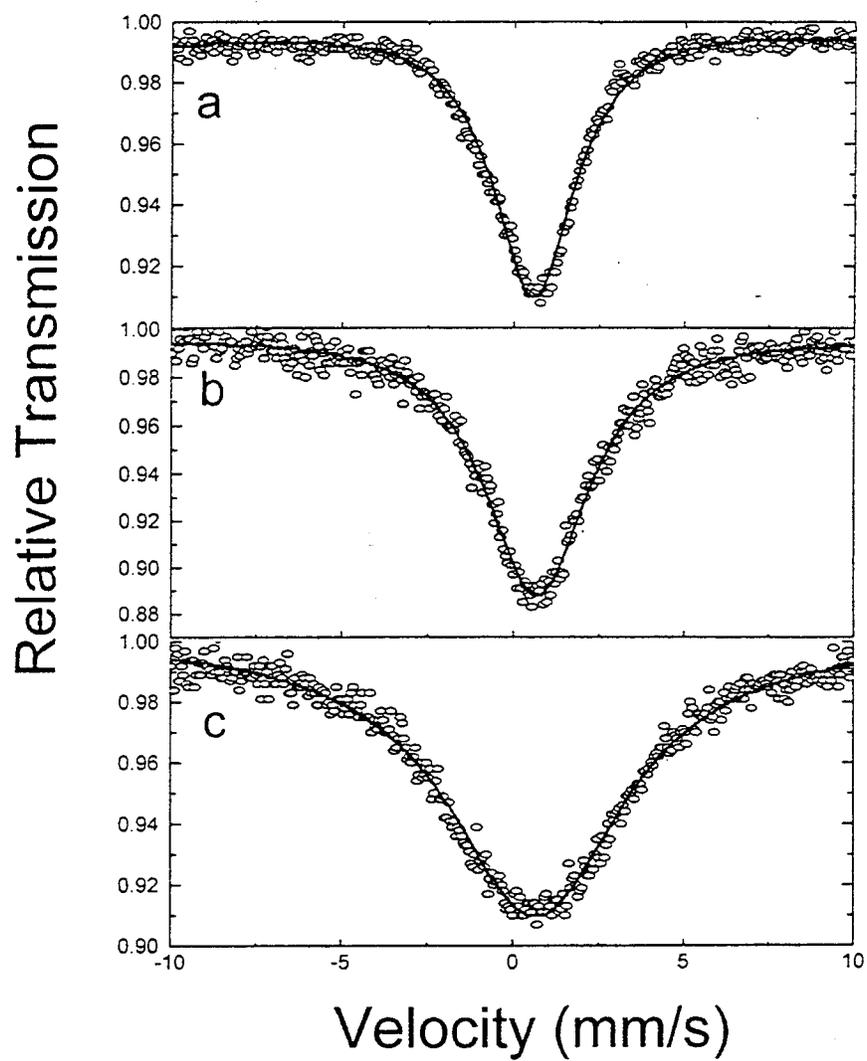


Figure 3. Temperature dependence of magnetic susceptibility.

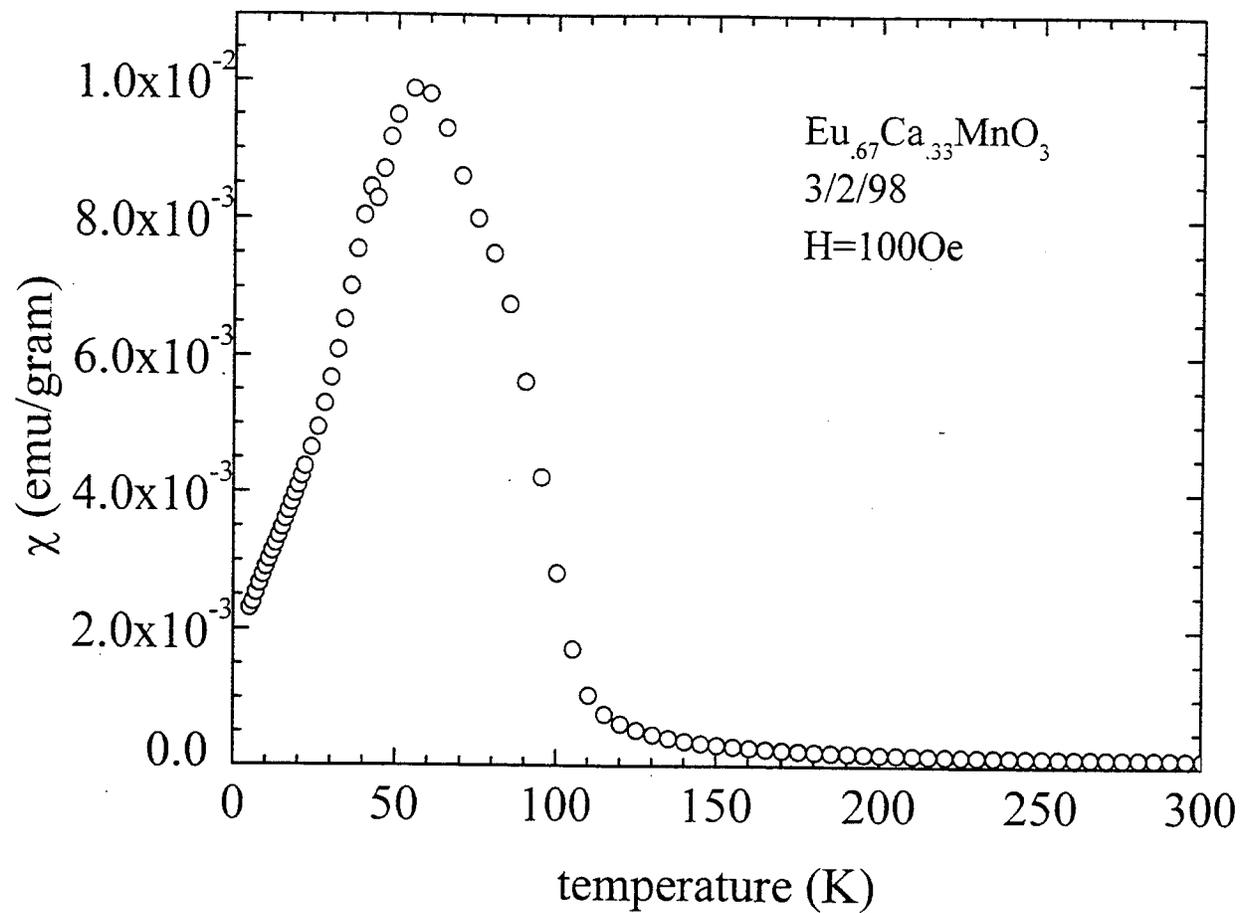


Figure 4. Transition temperature versus ionic radius of the A site for the strontium series.

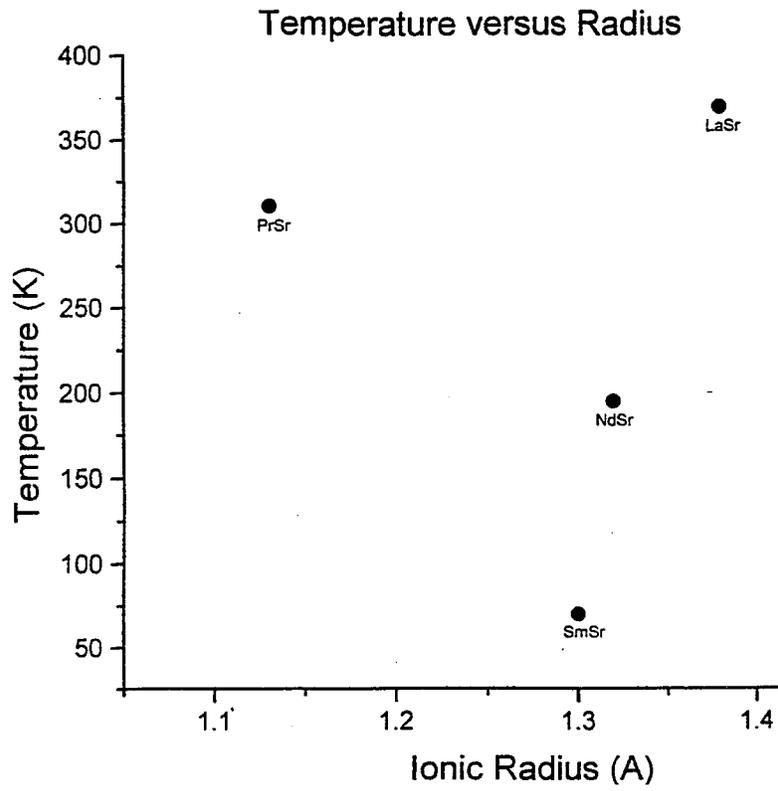


Figure 5. Transition temperature versus ionic radius of the A site for the barium series.

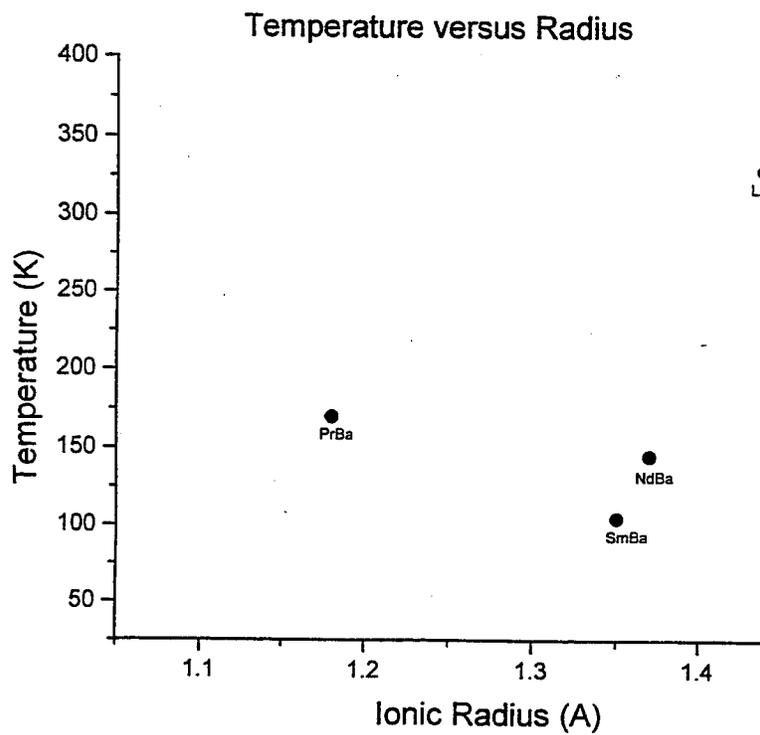


Figure 6. Transition temperature versus ionic radius of the A site for the calcium series.

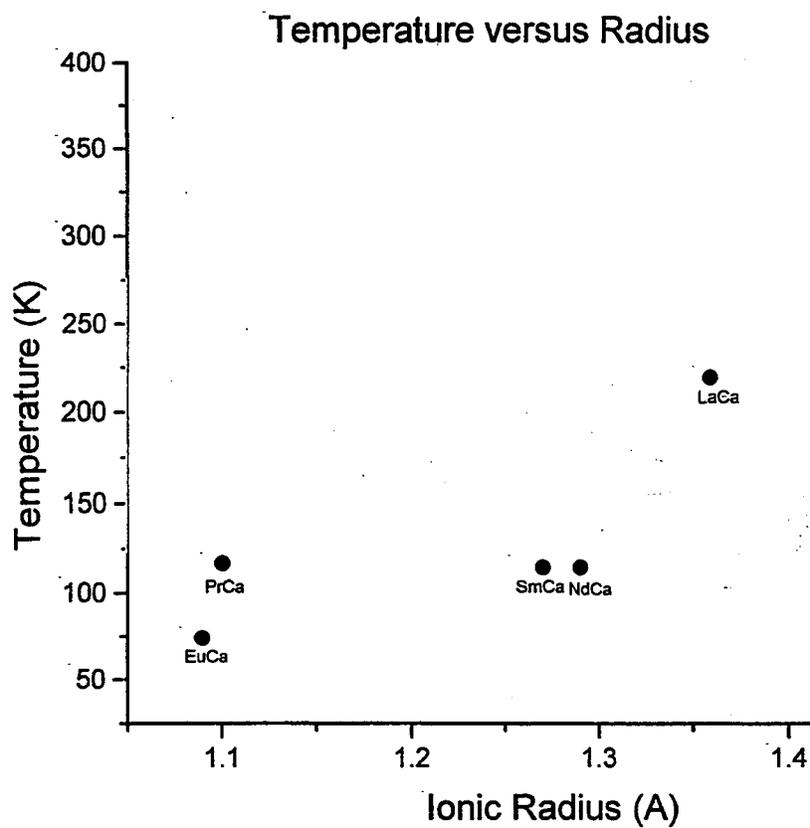


Figure 7. Transition temperature versus ionic radius of the A site for the lead series.

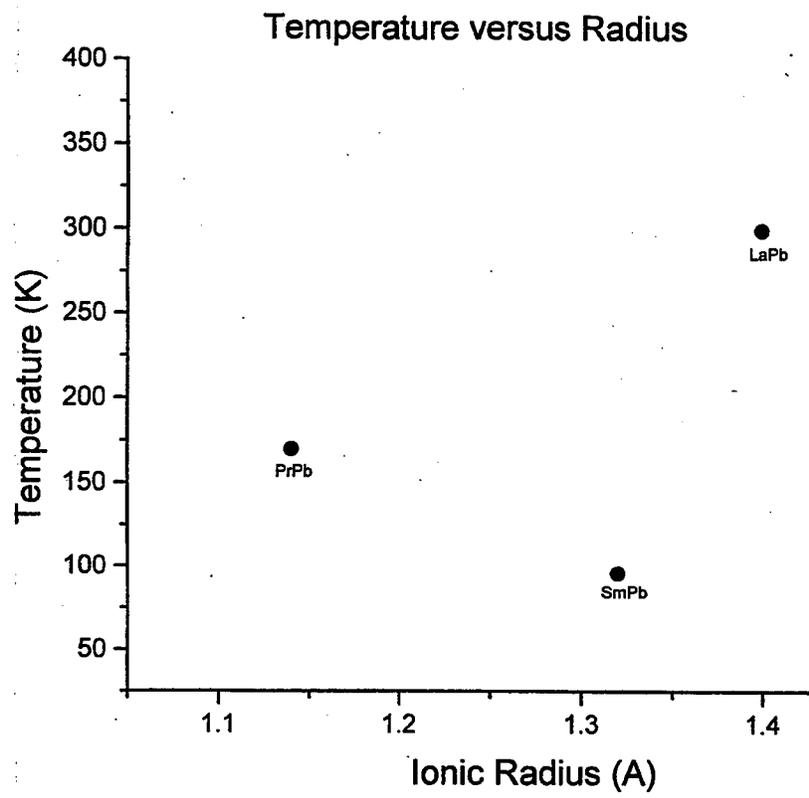


Figure 8. Transition temperature versus mass for the calcium series.

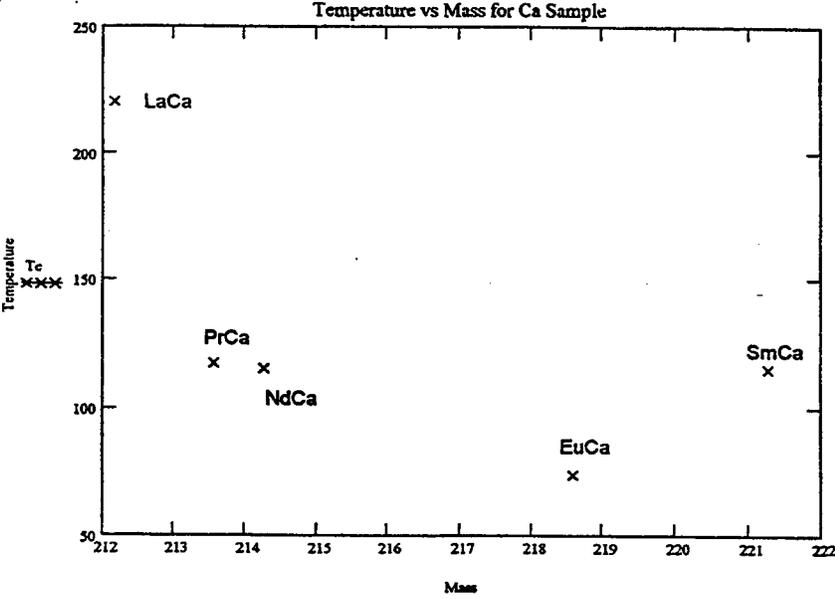


Figure 9. Transition temperature versus mass for the strontium series.

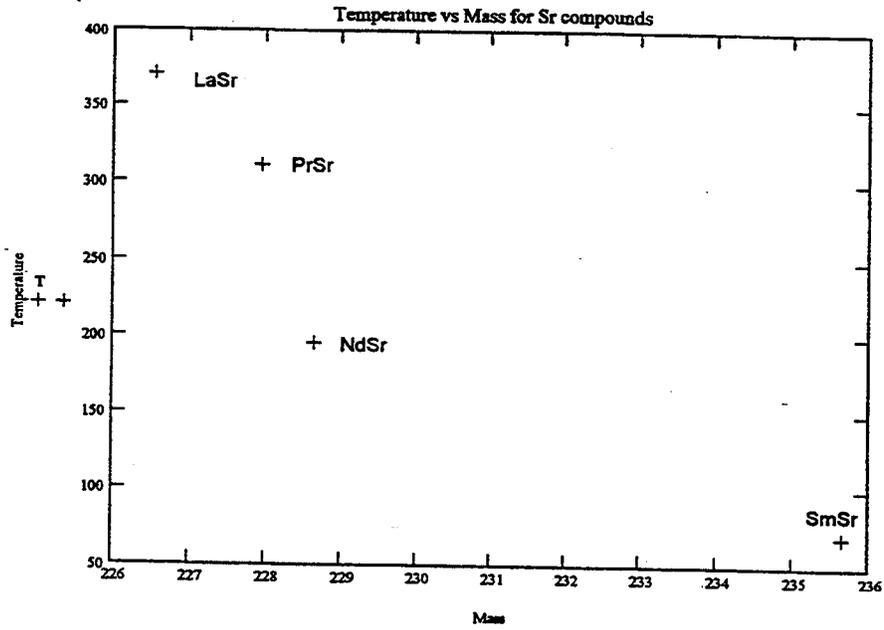


Figure 10. Transition versus mass for the barium series.

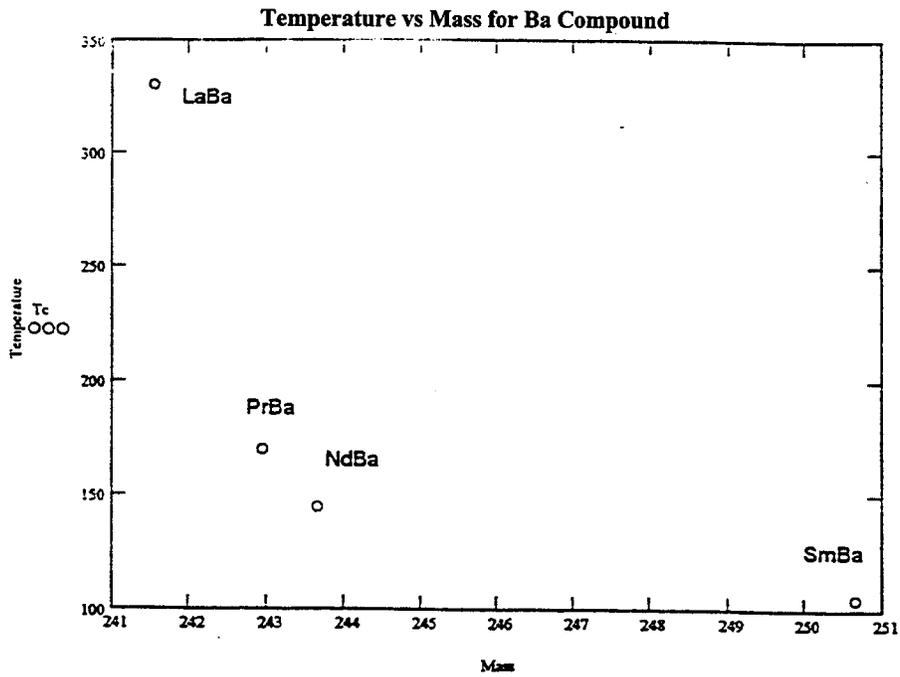


Figure 11. Transition temperature versus mass for the lead series.

